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TEXT-BOOK

OF

PHYSICAL CHEMISTRY

BY

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23. 2. 39.

NEW YORK
D. VAN NOSTRAND COMPANY
23 MURRAY AND 27 WARREN STREETS
1897

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Electrotyped by J. S. Cushing & Co., Norwood, Mass.

PREFACE.

Excepting the chapter on Phases, this book represents what I have been in the habit of teaching the Senior Class in the Chemical Course at Rutgers College. I find lectures very unsatisfactory. The subject needs much thought, and the student does not seem able to get the proper material for this from notes, unless the lectures are made mere dictations. Besides, Physical Chemistry has attained such development that it is well to put a certain part of it in permanent text-book form now, for whatsoever changes in our views time may bring, certain ideas we now have will not change. These fundamental ideas I have tried to put into this little book. Of course, I have also included some theories and ideas that later on may have to be rejected. That cannot be helped.

It is difficult to separate that which should be considered in a book of this kind from that which should be excluded. I have tried to give the most important principles, rather than mere facts, sometimes in the text, sometimes in the problems. As yet there are hardly any theories connecting light energy and so-called chemical energy; so light relations have been entirely omitted. For like reasons, crystallography has been omitted. It did not seem best to leave out matters which have been brought under strict discipline for the sake of

taking in those which have not yet been so organized. There is not room for both here.

I have not attempted to give a historical development of any subject, but have presented the subject in what I thought the clearest way, sometimes adopting one person's view in one part of a subject, another's view in another part, and perhaps my own in still another part. So I find it impossible in my lectures and in this book to state who was the first to develop any particular theory, or to discover any particular fact. I refer the student to Ostwald's *Lehrbuch d. Allgemeinen Chemie;* Nernst's *Theoretische Chemie;* Gibbs's *Equilibrium of Heterogeneous Substances; Zeitschrift f. Phys. Chemie.* All of these have been freely used in preparing this text-book.

I have adopted the view that matter is a collection of energies in space, considering the relations of the energies to be the prime object of investigation. With Ostwald, I feel confident that the materialistic interpretation has passed its prime and has no promise for the future. Still, as this is a text-book, I give the prominent materialistic views of the present time.

This book is intended for self-instruction of course, as well as for class-room use. Whoever works through it conscientiously, paying particular attention to the problems, will get a very fair idea of Physical Chemistry.

C. L. S.

September, 1897.

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TEXT-BOOK OF PHYSICAL CHEMISTRY.

CHAPTER I.

SOME GENERAL REMARKS ON ENERGY.

1. **Physical Chemistry.** — Physical Chemistry is the science which has for its object the investigation of chemical changes by physical methods.

2. **Chemical change.** — A chemical change is one in which the nature of the original body is very much changed.

3. **Force.** — That which can set a particle in motion or alter the velocity or direction of a particle already in motion is called force. Force can be created and destroyed.

4. **Energy.** — When a thing or a collection of things can be made to produce mechanical work, the thing or collection of things is said to contain energy.

That something which is directly involved in the doing of mechanical work, and which disappears in the doing of the mechanical work, is the energy. The characteristic of energy is its indestructibility.

5. **Matter.** — That which *seems* to cause a direct excitement of our senses we usually call matter. For instance, we move our hand around in space and it is suddenly arrested. We say it strikes the table. The sense of touch has been excited, and muscular effort stopped, apparently by the table. We see a book on the table. Our sense of sight has been excited. We cannot perceive anything between the book and our eye, and

so we say the book causes this excitement. We sit in front of a fire and feel warmth. Our sense of heat is excited. As we cannot perceive anything between us and the burning coals, we say the coals heat us.

The table, the book, the coals, are each the seat of an excitement. The table excites the sense of touch, the book excites the sense of sight, the burning coal excites the sense of heat.

It is only through such excitement that we perceive the existence of any object whatsoever. Hence we may define the different forms of matter as different collections of activities in space, the quality and quantity of these activities changing with the different forms of matter.

When we subject each and every such activity to a critical experimental examination, we find that it can be changed into mechanical energy; it corresponds, therefore, to the definition of energy. Hence we can define the different forms of matter as collections of forms of energy in space. This definition is free from any speculation; it rests on experimental evidence only.

If the collection forming any particular substance under investigation separates into two or more different collections, that particular substance is destructible.

Among the countless forms of matter which we know, there are only about seventy-five collections which do not separate into other collections, and consequently, in so far as they cannot be separated into other collections, they are to be considered indestructible. These collections are called elements. When we speak of a collection as being fixed, as being inseparable, we mean that there is one group of forms of energy going to make up that collection, each member of which cannot be separated, the one from the other. This is the essential group in the associated forms. There is another group, however, which is more or less accidental. For instance, consider a fixed quantity of oxygen. This has a certain amount of chemical energy, electric energy, distance energy, as compared with some stand-

ard, as hydrogen, under the same conditions, and cannot be changed without affecting the properties of the oxygen. These are the essential forms of energy, but the quantity of superficial electric energy it may contain depends upon the external conditions, and does not affect the individuality of oxygen. The essential forms of energy we mean when we speak of indestructible or undecomposable collections.

It is, however, very probable that sooner or later each of these seventy-five collections will be separated into other collections, some of the new collections being identical, and the number of undecomposed collections therefore greatly reduced. We cannot, however, believe that all the seventy-five collections will ultimately be reduced to one or more single separate forms of energy, because in that case we should have nothing left to account for the collection of forms of energy in space. We need energy and a something to enable energy to collect in space before we get a material substance. This something which enables, and perhaps causes, the energy to collect in space we shall call matter. The dissimilarity in the innumerable substances known to us come from the differences in the natures and proportions of the forms of energy collected in space.

Though the undecomposable collections called elements cannot be separated into other collections, they can be made to disappear by combination. We select oxygen and hydrogen and identify them by their energies. We then subject the mixed gases to the proper conditions and we get water. The collection known as water is very different from either collection known as oxygen or hydrogen, or a physical mixture of oxygen and hydrogen; no one could recognize oxygen or hydrogen in water. Consequently if we are to follow the line of the preceding argument we must agree that oxygen and hydrogen have actually been destroyed. So in all other cases in which elements combine. Consequently there are no collections of forms of energy which cannot be changed in some

way or another, and we can only say that certain collections cannot be *separated* into other collections, but not that they cannot be changed.

It follows from this that we cannot expect to separate the water into two or more collections different from the original collections that went to produce the water, different from the oxygen and hydrogen. This has led to the belief that oxygen and hydrogen still persist, as such, in water, and in general that the elements persist in a compound. This is not justified. All we may assume is that the conditions that *cause* the breaking up of a collection *require* the formation of those collections which went to make the collection just destroyed. But to claim that these collections originally existed in the collection that broke up is entirely opposed to the evidence of our senses. The explanation of the fact of our always getting certain collections from certain other collections is to be sought in the conditions that cause the breaking up; not in the assumption that the collections obtained previously existed in the collection producing them. We should not think for an instant that all the changes to which we can subject a body in any wise approach all the changes possible in nature. Until we have learned how to make all these changes possible to nature, we are not in a position to claim that any collection of energies is so fixed in association that it cannot in any wise be dissociated.

When we consider the relative quantities of two or more collections which combine to form another collection, we find fixed relations between the quantities of the collections of forms of energy which react to form the new collection.

In ordinary chemical language we say chemical reaction takes place between definite weights of matter. In our language we should say the relation between the intensities of the distance energies (gravity energies) of two or more collections reacting to form another definite collection is fixed.

When two substances combine in more than one proportion to form two or more bodies, in ordinary chemical language we

should say the ratio of the varying substance to the fixed substance is in general more or less simple. In our language we should say when two collections are capable of uniting to form more than one new collection by their union, the ratio of the intensity of the gravity energy in the varying collection to the intensity of the gravity energy in the fixed collection is in general more or less simple.

These two facts can be explained by two theories:

(1) By the atomic theory, which states that chemical reaction takes place between definite particles of matter, called the atoms, which cannot be further separated by any means known to us.

(2) By the energy theory, which says that a collection of energies can only be in equilibrium when there is a fixed relation between all the associated forms of energy. Consequently when two collections combine and form a third collection, they can only do so in the proportion that keeps the relation between all the forms existing in the third collection fixed. Now we may take the intensity of the gravity energy in any collection as measuring the other forms in that collection, for the relations between the forms of energy in a collection cannot be changed without destroying the identity of that collection. That is, if we have two collections, one containing two dynes of gravity intensity, and the other four dynes of gravity intensity, then if the two collections are alike, we must have twice as much of all the other forms of energy in the second case as we had in the first case. Therefore chemical change must take place between definite masses of matter, as measured by distance energy in the form of gravity energy.

We could also have used kinetic energy as a measure of the other energies, instead of distance energy.

Now as several associated forms of energy can have more than one equilibrium, we may expect to find that two collections will react, under different conditions, to form two or more different collections. This is the case. In the atomic theory

this fact is announced in the law of multiple proportions, though the simplicity in the ratios as announced in that law is illusive.

We see then that we cannot only express our ideas of matter in terms of energy, but also that we can find the fundamental fact of the atomic theory, the law of definite proportions, in the condition of equilibrium between the energies in a group of associated forms of energy.

We shall pass on now to a somewhat detailed consideration of the forms of energy, remembering that matter is to be considered as that something which enables forms of energy to collect in space.

6. **Energies.** — The forms of energy which are recognized at the present time are :

I. Mechanical energies.
  a. *Kinetic energy.*
  b. *Space energies.*
    α. Linear energy (distance energy).
    β. Surface energy.
    γ. Volume energy.

II. Heat energy.

III. Electrical energy.

IV. Magnetic energy.

V. Radiant energies.
  a. *Radiant heat energy.*
  b. *Radiant light energy.*
  c. *Roentgen ray energy.*

This classification is somewhat artificial ; we know too little to make a natural classification.

Under mechanical energy we put those forms of energy which have been hitherto expressed in terms of matter. That is, they do not seem to require any very peculiar condition in a system for them to become evident; they become evident

without any chemical or electrical treatment. Obviously such arrangement is artificial, but it is convenient enough, and so we use it.

7. **Kinetic energy.** — The first of the mechanical energies, kinetic energy or that form of energy in an associated group of energies which is manifested when the group moves from place to place, is so well known, that we shall pass it by, merely giving its analytical expression,

$$K = \tfrac{1}{2} m v^2,$$

where K is the kinetic energy, m that which is commonly called the mass of the collection of energies, and v the velocity with which the collection moves. Its dimension is

$$K = E,$$

where E is energy in general.

The *dimension* of a quantity is the expression of that quantity in the fundamental units of measurement. We shall choose as these units, time, space, and energy. Hence as K is an energy and nothing more, it has the simple dimension E.

8. **Space energy.** — *Linear energy: distance energy.* As we let any collection of energies above the earth's surface move from one place to another place nearer the earth's surface, we find that energy is produced in the operation. This collection loses gravity energy; we gain it. Hence every collection of forms of energy above the earth's surface is connected with a form of energy which is dependent upon the distance between the earth's surface and the collection under consideration. The distance is a linear quantity, and therefore gravity energy is called a linear energy. The ordinary expression for work, force, and distance shows that mechanical work is a linear energy. Its analytical expression is

$$L = lf,$$

where L is the linear energy, f is a force, and l the distance through which the force acts.

In the case of G, gravity energy, l becomes the height h, above the earth's surface, and f becomes the weight, w; so

$$G = hw.$$

Its dimension is $G = E$;

likewise $L = E$.

We assume that h is not great enough for w to change appreciably.

There are a good many linear energies. In one respect electrical and magnetic energies are linear energies; for the energy in a system composed of two electrified bodies, or magnets, is partly determined by the distance between them. Still in many other respects these energies are more than linear energies, and it is more convenient to put them in a class by themselves; possibly they are compound energies. A compound energy is a group of associated forms of energy, excluding gravity energy, or any other form of energy which when associated with the other forms would make matter.

9. **Surface energy.** — When we try to increase the surface of a liquid, we find that energy is required to do this, and if after increasing the surface we leave it alone, the surface contracts so that energy is lost by the liquid. This energy at the surface of a liquid is called surface energy. It is probably of great importance in the phenomena of life, but the chemist so far has had little to do with it. Possibly it is also a compound energy. Its analytical expression is

$$S = \gamma s,$$

where S is the surface energy, γ a constant, and s the surface that disappears or is formed. Its dimension is

$$S = E.$$

10. **Volume energy.** — This energy is of great importance in the use of gases or vapors. It is involved in every operation of the steam engine. It is an energy which permits an expan-

sion against an opposing energy. An opposing energy is an energy which tends to cause the energy which it opposes to change into some other form of energy.

The volume energy resulting from the expansion of solids and liquids has not been found very useful. The change in volume under the required conditions is usually too small to enable the energy to be used. Blasting by the explosion caused by adding water to calcium oxid is one of the few examples.

The volume energy resulting from the expansion of gases is, however, of great use, for the change in volume can be made about as we choose, to fit our machines.

The analytical expression of volume energy is

$$V = pv,$$

where V is the volume energy, p the pressure, and v the change in volume. Its dimension is

$$V = E.$$

11. **Heat energy.** — This form of energy is involved directly or indirectly in most of the changes of energy known at present. It is seldom possible to change one form of energy into another form without some energy appearing as heat. This may be because the heat energy exists in all the common energies, which we are not at all justified in assuming, or it may be because heat energy is a form of energy which many other forms of energy must assume, either wholly or in part, when changing from one form of energy to another.

Its analytical expression is

$$Q = Ht \text{ or } Q = Tq,$$

where Q is the heat energy, H a unit quantity of heat, t the change in temperature, q the change in quantity of heat, T the absolute temperature. Its dimension is

$$Q = E.$$

12. **Electric energy and magnetic energy.** — The consideration of electric energy in its relation to chemical change will come

later. There is nothing to be said about it now. Magnetic energy we shall pass by altogether. Their analytical expressions are

$$\mathrm{E} = \epsilon V \text{ and } M = \mu V,$$

where E and M are the electrical and magnetic energies respectively, ϵ and μ electrical and magnetic quantities respectively, and V the change in electric potential or magnetic potential. The dimensions are

$$\mathrm{E} = E \text{ and } M = E.$$

13. **Radiant energy.** — A consideration of this energy in any detail is beyond the scope of this work. A few words will be said about it later. Its analytical expression is

$$\mathrm{R} = er,$$

where R is the radiant energy, e, coefficient of emission, and r, intensity of radiation. Its dimension is

$$\mathrm{R} = E.$$

14. **Factors of the energies.** — Let us put down the analytical expressions of the energies again.

Energy.	Analytical Expression.	Factors.	
		Capacity.	Intensity.
Kinetic energy	$\frac{1}{2}mv^2$	$\frac{1}{2}m$	v^2
Linear energy	lf	l	f
Gravity energy	hw	h	w
Surface energy	$s\gamma$	s	γ
Volume energy	vp	v	p
Heat energy	Ht or qT	H or q	t or T
Electric energy	ϵV	ϵ	V
Magnetic energy	μV	μ	V
Radiant energy	er	e	r
Internal energy	—	—	—

When we examine the conditions of equilibrium for a system containing one or more of these energies, we find that equilibrium is always determined by one of the two quantities which make up an energy, and always by the same quantity for the same energy. For instance, the heat in a kilogram of water is in equilibrium with the heat in a gram of water when the temperature of each is the same; two bodies with vastly different kinetic energies do not disturb each other when moving in the same direction if their velocities are the same. Volume energy in a gas is in equilibrium with the volume energy in another gas when the pressure in each is the same. This quantity which determines the equilibrium is called the *intensity* of the energy. The other quantity is called the *capacity* for the energy. These two quantities, whose product is the energy, are called the *factors* of the energies. They are given in the last two columns of the table above.

We therefore have for the analytical expression of an energy

$$E = ci.$$

where c is the capacity and i, the intensity.

Hence, when the quantity of an energy changes and c is constant,

$$\frac{dE}{di} = c. \qquad 1$$

When the quantity of an energy changes and i is constant,

$$\frac{dE}{dc} = i. \qquad 2$$

The reader will observe that the mass of a body may be defined as one half its capacity for kinetic energy; that force may be defined as the intensity of linear energy; and so on.

Equations 1 and 2 enable us to determine the absolute value of the constant factor when the other factor is variable.

For instance, with kinetic energy we can make an experiment

corresponding to equation 1 and so get the absolute value of the capacity m.

$$m = \frac{1}{v}\frac{dK}{dv}.$$

But we cannot carry out an experiment corresponding to 2; namely,

$$v^2 = 2\frac{dK}{dm},$$

for the mass of a moving body is not altered by kinetic energy.

In the case of gravity energy, 2 is applicable, and we get the absolute value of the intensity, the weight,

$$g = \frac{dG}{dh}.$$

We assume that h is so small that w does not sensibly change.

15. **Conditions of equilibrium.** — Two opposing energies of the same kind are in equilibrium when their intensities are equal.

Two opposing energies of different kinds are in equilibrium when an infinitesimal increase of one energy necessitates an equivalent decrease of the other. That is, when

$$dE_1 = dE_2, \qquad 3$$

or when

$$d(i_1c_1) = d(i_2c_2), \qquad 4$$

where i_1, c_1, and i_2, c_2, are respectively the factors of the two energies, E_1, E_2.

To apply these equations we must know the relations between the two opposing energies.

For instance, suppose we wish to determine the condition of equilibrium in the case of a cylinder containing a gas which supports a piston with a weight. The two energies involved are volume energy and linear energy, hence equation 4 becomes

$$d(pv) = d(fl). \qquad 5$$

For an infinitesimal change the two intensities (p and f) are to be considered constant, and so

$$pdv = fdl,$$

where dl is the distance the piston moves when the volume increases by dv. The relation between the volume energy and the linear energy, which in this case we suppose to be gravity energy, is

$$dv = adl, \qquad 6$$

where a is the area of the piston. Substituting, we get as the condition of equilibrium

$$pa = f; \qquad 7$$

that is, the force with which the weight presses on the piston must equal the pressure of the gas times the area of the piston, or the intensity of the linear energy must be a times the intensity of the volume energy. In general, when two different energies are in equilibrium, there is a jump in the value of their intensities.

An equation which connects the variable factors of two energies is called the engine equation for those energies, so equation 4 is an engine equation.

An *engine* is an arrangement which changes one form of energy into another form.

Again, suppose we wish to determine the condition of equilibrium between volume energy and surface energy.

Equation 4 becomes

$$pdv = \gamma ds.$$

If we consider the case of a soap bubble, we have two surfaces, the inner and outer, and hence

$$pdv = 2\gamma ds. \qquad 8$$

The volume of the bubble is $4/3\,\pi r^3$, hence

$$dv = 4\pi r^2 dr;$$

the surface of the sphere is $4\pi r^2$, hence

$$ds = 8\pi r dr.$$

Substituting in 8,

$$p = \frac{4\gamma}{r}.$$

This is the condition of equilibrium.

16. **Persistence of the factors.** — When we compare the energies of a compound with the energies of the elements composing that compound before they have combined to form the compound, we find that the compound often contains less energy than the elements composing it contain, each taken separately. Usually this escaping energy passes off as either heat or electric energy, though sometimes as volume energy, as in explosions. What the original form of the escaping energy may be in the substance from which it escapes we do not know. We shall call it internal energy. Usually it is called chemical energy, but that term is not good, for it implies a new energy, and we have no evidence of any energy involved in chemical action other than those given in the list on page 6. We do not mean that there is no such thing as chemical energy, but we have no evidence of it.

After chemical reaction we find that some forms of energy are lost to the system, some are retained. Internal energy usually is lost, but gravity energy persists. Likewise some capacities persist, as the capacity for kinetic energy. This capacity is the same in the compound as in the elements.

17. **Measurement of energy.** — We have no absolute measurement of energy, for we do not know what energy is in its essence, but we can measure all forms of energies by changing them directly or indirectly into one common form. The form chosen is usually kinetic energy or gravity energy. That is, we state that so many grams will be raised so many centimeters against gravity energy by the energy to be measured, and if an intensity of an energy — not an intensity factor —

is desired, we add the number of seconds required to do this. When the gram is raised against gravity, 981 units of force or dynes are involved, and so we can reduce the weight of a gram still further by multiplying the measure obtained from raising a gram by 981. This gives the energy in the simplest units that we have found convenient. They are commonly called the *absolute units*, and denoted by c.g.s. (centimeter, gram, second).

The gram here means the mass of 1 cc. water at 4°, and the absolute unit of force or dyne is the force that gives this mass a velocity of 1 cm. per second after acting for 1 second. Gravity force gives a gram mass a velocity of 981 cm. per second after acting for one second.

18. **Available energy.** — When one form of energy changes into another form, that portion of energy that passes into a certain desired form of energy is called the *available* energy.

CHAPTER II.

GASES.

19. **Volume energy.** — We have defined volume energy as the energy which permits an increase in volume. As every change in volume involves volume energy, it is a very common energy.

The connection between the volume energy coming from the expansion of solids and liquids, as such, and other forms of energy, seems to be so complicated by the other forms in the solids and liquids, that we have not learned much about volume energy from the study of these bodies.

The volume energy coming from the expansion of gases is much purer, much less closely connected with other forms of energy, so that the study of gases has thrown much light upon the relations of other forms of energy to volume energy, for we can impose conditions with gases that will bring out the characteristics of the forms involved, without fearing any complication from other forms of unknown action.

20. **Perfect gas.** — We shall define a perfect gas as a collection of forms of energy in which the volume energy is not opposed by any other form of energy. In so far as the volume energy is opposed by some other form, the collection varies from a perfect gas. We do not know of a perfect gas, unless helium or argon should be one; the nearest approach to perfection is in hydrogen, oxygen, nitrogen, helium, and argon. So a perfect gas is an ideal thing.

21. **Factors of volume energy.** — The factors of volume energy are pressure and volume, the first being an intensity, the second a capacity. The volume energy in a perfect gas does not

change with the volume; for the product of the two factors is constant; that is,

$$p_1 v_1 = p_2 v_2 = p_0 v_0 = \text{constant}. \qquad 9$$

This is the analytical expression of Boyle's law. The standard pressure and volume are denoted by p_0 and v_0 respectively. The pressure $p_0 = 76$ cm. Hg, or as the sp. gr. of Hg is 13.6, we get $p_0 = 76 \cdot 13.6$ gravity units, or $76 \cdot 13.6 \cdot 981$ dynes. The v_0 is to be referred to a grammolecule of gas. A *grammolecule* of a gas is the weight in grams numerically equal to its molecular weight. As, according to Avogadro's law, equal volumes of gases at same temperature and under same pressure contain equal number of molecules, the volume of a grammolecule of H is the volume of a grammolecule of any gas. The volume v_0 is to be measured at p_0 and 0° C. A liter of H weighs $0.0896 = 0.09$ grams, so $v_0 = 2/0.0_4 9 = 22222$ cc. at 0°, or at any temperature $v_0 = 22222\ T/273$, where T is the absolute temperature. Hence

$$pv = p_0 v_0 T/273 = \frac{76 \cdot 13.6 \cdot 981 \cdot 2}{0.0_4 9 \cdot 273} T = RT = 82510000\ T. \qquad 10$$

The numerical value of R is obvious.

In determining the available energy in the expansion of a gas at constant temperature, we must remember that, as the intensity changes with the capacity, the product of the two factors only gives the true available energy when the change in one factor is so small that the value of the other factor may be considered constant. Then

$$dE = vdp = pdv = dW, \qquad 11$$

where E is the available energy, and W its value in linear energy.

For a finite quantity of linear energy or work, we have

$$\int_{W_1}^{W_2} dW = \int_{v_1}^{v_2} pdv. \qquad 12$$

Substituting from 10, and integrating,

$$W = RTl\frac{v_2}{v_1}. \qquad 13$$

In all these changes T is kept constant by supplying the necessary heat from without. A change in which T is constant is called an *isothermal* change.

The volume energy of a perfect gas is a *persistent* energy. When we attempt to get work from the volume energy of a gas, we find that the work we get comes from heat energy, or some other energy, and that *so long as the gas remains a perfect gas and its mass does not change, so long the volume energy of the gas remains constant, whether T changes or not.* The volume energy is therefore an energy which stands between heat energy or some other energy and mechanical energy, but volume energy in a perfect gas does not itself directly change into mechanical energy.

22. **Mechanical theory of gases.** — The direction of past and present scientific thought being so strongly towards the materialistic view of things as opposed to the energy view, we cannot leave the subject of gases without at least glancing at the prevailing materialistic ideas concerning them.

Gases are supposed to consist of minute independent particles in constant motion. The independence is perfect in a perfect gas, imperfect in an imperfect gas. These particles correspond to the molecules of the chemist. Pressure is the result of blows from the molecules. Consequently a vessel containing a gas should grow warm on account of the kinetic energy of the molecules changing into heat energy. As this does not happen, the molecules of gas and vessel must be perfectly elastic, for only in this way can we explain why the kinetic energy stays with the molecule. This is one of the weak points of the theory.

Let the temperature be constant. Let m be the mass of a molecule, u its velocity. The velocity is dependent only upon the temperature and nature of the gas. As the velocity is in an

unknown direction at any instant, let us decompose u into the three directions of space, x, y, z. Then

$$u^2 = x^2 + y^2 + z^2.$$

As the molecules of gas and vessel are perfectly elastic, the effect of an impact is represented by the double momentum $2mx$, $2my$, $2mz$, according to the direction considered. Suppose the gas is contained in a cube whose sides are parallel with the directions of space and of the length l. Then the number of impacts of a molecule in a second on each two opposite walls of the cube are respectively x/l, y/l, z/l. The effect of these impacts during one second is respectively

$$\frac{2mx^2}{l}, \quad \frac{2my^2}{l}, \quad \frac{2mz^2}{l},$$

and the total effect produced by a molecule during one second is

$$2m\left(\frac{x^2}{l} + \frac{y^2}{l} + \frac{z^2}{l}\right) = \frac{2mu^2}{l}.$$

Let n be the number of molecules in the cube. Then the total effect of all the molecules on the walls of the cube during a second is

$$\frac{2mnu^2}{l}.$$

This is equivalent to the total pressure; but, as the pressure is usually referred to a unit area, we divide by the surface of the cube, $6l^2$; so

$$\frac{2mnu^2}{6l^3} = \frac{1}{3}\frac{mnu^2}{v} = p,$$

or

$$pv = \tfrac{1}{3}mnu^2 = \frac{2}{3}\frac{mnu^2}{2}. \qquad 14$$

This equation applies to a cube. The molecules are so very small that the cube we have just considered can be very small, so small that a vessel of any shape may be considered as composed of an accumulation of these very small cubes. Hence, as 14 is true for each cube, it is true for the vessel made up of these cubes, and therefore is true for any vessel.

Equation 14 shows that the product of pressure and volume is 2/3 the kinetic energy in the gas. Accordingly, when we wish to pass from the kinetic theory to the energy theory, and wish to determine the volume energy in the gas, we must take 2/3 the supposed kinetic energy. The student understands that these numbers which connect the expressions for different energies come from the selection of units. Forms of energy are strictly equal, and two units of one form cannot equal three units of another form unless the units which measure each energy are different.

We see that for a given mass of gas at constant temperature pv is constant. This is Boyle's or Mariotte's law.

We find from experience that when v is constant, p changes as the absolute temperature; hence, from 14 the kinetic energy changes as the absolute temperature. The absolute temperature is measured by the kinetic energy of the gas.

Two molecules in a system such as we are considering are in equilibrium when the kinetic energies are equal. So for equal volumes of two gases at the same pressure and temperature,

$$\frac{2}{3}\frac{m_1 n_1 u_1^2}{2} = \frac{2}{3}\frac{m_2 n_2 u_2^2}{2},$$

and so $n_1 = n_2$. This is Avogadro's law.

Such, in brief, is the mechanical or kinetic theory of gases.

There are several very serious objections to it. In the first place, a perfect elasticity in a molecule cannot be explained, for our experience with elastic bodies compels us to accept complexity of structure in elastic bodies, and molecules of gases are sometimes too simple in their structure to admit of elasticity as we understand it. If, nevertheless, we insist that the molecules are elastic, we are driven back to a vague vortex theory of the ether. Besides this, we can only deal in mean velocities, mean pressures, and so on; the molecules are too small and numerous for any separate treatment. This leads to troubles in other directions. The kinetic theory is a trouble-

some thing and is becoming an object of ridicule. It has never directed the chemist to any new discovery or idea, unless it may be Van der Waals' theory, and that would probably have come any way.

23. **Van der Waals' theory.** — Before we leave the subject of gases we must consider one other theory, that of Van der Waals.

When we raise the pressure on a gas greatly, we find that Boyle's law no longer expresses the relation between pressure and volume even approximately; the pressure increases much more rapidly than the volume diminishes.

The energy theory says that this is because the factors of the volume energy in imperfect gases are not inversely proportional. For moderate intensity they are inversely proportional, but when the intensity is high, the factors are no longer inversely proportional.

The kinetic theory says that the molecules occupy space; that this space is small and may be neglected when the volume of the vessel containing the gas is relatively large, that is, when the pressure is low; but that the volume occupied by the molecules is very appreciable when the total volume is small, and, therefore, pressure is high. Consequently v must be changed to $v - b$, where v is the volume of the vessel, and b the volume required by the molecules, so that $v - b$ is the available volume: b seems to diminish with the pressure. Moreover, as there is evidence of mutual interaction between the molecules when they are brought close together, p must be changed to $p + a/v^2$, where v and p have the same value as before, and a is a constant. So 10 becomes

$$\left(p + \frac{a}{v^2}\right)\left(v - b\right) = \left(p_0 + \frac{a}{v_0^2}\right)\left(v_0 - b\right)T = RT, \qquad 15$$

where R now has a value evidently different from its value in 10.

This equation has given some very interesting and valuable

results. Originally derived from the kinetic theory of gases, it has nevertheless none of the absurdities of that theory and will not fall with it. Van der Waals' equation, 15, expresses an action and is independent of any theory.

24. **Critical quantities.** — When we compress any gas below a certain particular temperature very strongly, we find it condenses to a liquid, though at a temperature slightly above this certain particular temperature it does not do so, though the pressure may be increased many times, so that at this higher temperature the density of the vapor may be considerably more than that of the liquid at a slightly lower temperature. The temperature at which the vapor first changes into liquid is called the *critical temperature,* the pressure is called the *critical pressure,* and the volume is called the *critical volume.* These three quantities we shall call the *critical* quantities.

We see that a collection of those forms of energy which we call a liquid can only exist when there is a certain relation between the intensity factors of heat energy and volume energy, as well as a certain maximum value of the heat intensity.

We may consider the two new terms of 15 as corrections for the volume energy factors when the intensity of the heat energy is relatively low, but yet not high enough to prevent the formation of liquid.

We cannot go into the discussion of 15; it would lead us too far from our subject of physical chemistry. But we may state that it is possible to express the critical factors in terms of a and b. If π_0, ϕ_0, θ_0 be respectively critical pressure, critical volume, and critical temperature,

$$\pi_0 = \frac{a}{27\,b^2},\ \phi_0 = 3\,b,\ \theta_0 = \frac{8}{27}\cdot\frac{a}{bR}. \qquad 16$$

If we write pressure, volume, and temperature in terms of their critical values, we get from 15 and 16

$$\left(\pi + \frac{3}{\phi^2}\right)\left(3\,\phi - 1\right) = 8\,\theta, \qquad 17$$

where $$\pi = \frac{p}{\pi_0},\ \phi = \frac{v}{\phi_0},\ \theta = \frac{T}{\theta_0}.$$

This equation is applicable to all gases and liquids, and seems to express their behavior very accurately, though there is some dispute regarding its validity.

When two gases are at pressures and temperatures which are equal multiples, respectively, of their critical pressures and temperatures, they are said to be in *corresponding states.*

We may define a gas *as an aëriform state of matter above its critical temperature;* a vapor, *an aëriform state of matter below its critical temperature.* This distinction is not always made, however; vapor and gas are terms used synonymously by many writers.

CHAPTER III.

HEAT.

25. **Units of heat.** — We use three units: the thermal unit, called calorie, and two mechanical units, the gravity unit and the absolute unit. The first is the heat required to raise the temperature of 1 gram of water 1°. It is equal to 42750 grams raised 1 cm. high. As the force of gravity is 981 dynes,

1 calorie = 42750 gravity units = $42750 \cdot 981 = 4194 \cdot 10^4$ ergs.

26. **Thermodynamics.** — Thermodynamics was originally the science of the relation of heat energy to mechanical energy. By usage the meaning has been broadened to include other energies besides mechanical energy. So thermodynamics is the science of the relations of heat energy to all the other energies.

27. **Internal energy.** — When heat energy is added to a substance, if the substance is properly situated, a part of the heat energy takes the form of external work, while the rest of the heat increases the internal energy of the substance, sometimes changing its temperature, sometimes not. When the substance is so situated that external work cannot be done, all the heat energy takes the form of internal energy. *Internal* energies are the forms of energy *inside* a collection of forms of energy. Consequently all the forms in a system are forms of internal energies until the system begins to lose energy, then some of the internal forms pass into external forms.

28. **Specific heat.** — The specific heat of a body is the quantity of heat required to heat a unit quantity of the body 1°.

In gases there are three specific heats to be considered: the true specific heat, the specific heat at constant volume, and the specific heat at constant pressure. When referred to gram-molecules, we call these specific heats molecular heats.

29. **First law of thermodynamics.** — If dQ is a differential of heat energy, we have by the law of conservation of energy,

$$dQ = dU + dW, \tag{18}$$

where dU is the portion of dQ which goes into internal forms of energy, and dW is the portion which goes to external work.

This equation expresses the *First Law of Thermodynamics as applied to heat energy.* It is the same in form as the law of the conservation of energy.

30. **Heating of solid and liquid.** — Let us add a quantity of heat dQ to a grammolecule of some solid which can be melted. A portion of the heat goes to change the temperature of the body by the quantity dT. This portion may be represented by $(\partial U/\partial T)dT$, where $\partial U/\partial T$ is the rate of change of internal energy with the temperature. Another portion of the heat goes to change the volume by the quantity dv, so that we have $(\partial U/\partial v)dv$, as the change in internal energy due to change in volume dv, where $\partial U/\partial v$ is the rate of change of internal energy with the volume. If the solid be subject to a pressure p, and this is usually the case, we have for dW, the work pdv. Substituting in 18, we get

$$dQ = \frac{\partial U}{\partial T}dT + \left(\frac{\partial U}{\partial v} + p\right)dv. \tag{19}$$

In the case of a solid, pdv is usually negligible, so

$$dQ = \frac{\partial U}{\partial T}dT + \frac{\partial U}{\partial v}dv. \tag{20}$$

When the volume is constant, 19 reduces to

$$\frac{dQ}{dT} = \frac{\partial U}{\partial T}. \tag{21}$$

The first member of this equation is the molecular heat of a body at constant volume.

According to a theorem of Clausius, which we cannot discuss in this book, though a very excellent theorem, the molecular heat at constant volume, of any substance, is constant, whatever the state of the substance may be; the difference in the molecular heats in the different states being due to a use of heat in some work other than heating the body. To distinguish this heat from the ordinary molecular heat, Clausius calls it the *true molecular heat.* We denote the molecular heat at constant volume by C_v. We can determine the true molecular heat of any substance that can be changed into a perfect gas; for as we shall see, in that state, $\partial U/\partial v$ is zero, so from 21, where v is constant and the body is a perfect gas,

$$\frac{\partial U}{\partial T} = \frac{dQ}{dT} = C_v. \qquad 22$$

Therefore we may write 20 thus,

$$dQ = C_v dT + \frac{\partial U}{\partial v} dv, \qquad 23$$

which gives us the change of internal energy with the volume.

As we continue heating the solid, a time comes when the body changes suddenly. The heat energy then changes entirely into those forms of internal energy which characterize liquids, none of it remaining in the form of heat; consequently there is no change in temperature until the solid disappears. We say the solid melts. The total quantity of heat required to melt a grammolecule of solid is the molecular heat of fusion. In this case, 20 becomes

$$dQ = \frac{\partial U}{\partial v} dv, \text{ or } \frac{dQ}{dv} = \frac{\partial U}{\partial v}, \qquad 24$$

which gives the change of internal energy with the volume on melting.

Equations 20 to 23 are directly applicable to liquids, so long as vaporization is prevented.

Suppose that the liquid be heated to its boiling point without letting it vaporize. Then let it vaporize entirely, but not do any external work; that is, let it vaporize into a vacuum. Under these conditions vaporization corresponds to fusion, and equation 24 is directly applicable.

When, however, the vaporization is not into a vacuum, but against a pressure p, as dv is appreciable compared with dQ, we can no longer neglect pdv in 19, and we have for the heat of vaporization

$$dQ = \frac{\partial U}{\partial v} dv + p dv, \qquad 25$$

which gives the change in internal energy with the volume when the liquid vaporizes and external work is done isothermally.

Vaporization is a much more interesting change from the energy point of view than fusion. The changes in energy in fusion are not very marked, but in vaporization the change is strongly marked by a large amount of volume energy.

31. **Heating of vapor and gas.** — Continue to heat the vapor, and assume that it does not decompose at the highest temperature considered. Equation 19 is directly applicable when the gas is allowed to do external work. When external work is prevented, v is constant, 19 reduces to 21, and gives the molecular heat of the vapor at constant volume. When we compare the molecular heats at constant volume for a gas at different temperatures, we find the values are not alike. With hydrogen, oxygen, and nitrogen, and probably with helium and argon, the difference is slight — so slight, indeed, that one might think that it came from the error of experiment. With other gases the difference is greater. So likewise for molecular heats at different volumes, but at the same temperature. Strictly speaking, therefore, in no known case can heat energy be changed completely into volume energy. Only in the

imaginary case of a perfect gas is the molecular heat at constant volume strictly independent of volume and of temperature.

From 14,

$$\frac{mnu^2}{2} = \tfrac{3}{2}\,pv = \tfrac{3}{2}\,RT = \tfrac{3}{2}8251 \cdot 10^4\,T = 123765 \cdot 10^3\,T \text{ ergs.}$$

This gives the kinetic energy in a grammolecule of gas at T. For each degree the volume increases by 1/273d of its volume at 0°, and consequently the kinetic energy increases for each degree by

$$\frac{123765 \cdot 10^3 \cdot 273}{273} = 123765 \cdot 10^3 \text{ ergs;}$$

for $T = 273$, since the initial volume is measured at that temperature. In calories this is

$$\frac{123765 \cdot 10^3}{42750 \cdot 981} = 2.95 \text{ cals.}$$

This should be the molecular heat at constant volume of any gas if all the heat energy that went into the gas went to raise the temperature. There are few, if any, gases that have so low a molecular heat as this, though possibly argon and helium have. So we must conclude that in most gases, at least a part of the heat energy used to heat them is changed into other forms of energy; that is, if we accept the kinetic theory of gases.

When we examine the relations between pressure and volume for a vapor, we find that so long as the temperature is neither very far above the point of liquefaction nor very near it, and the pressure near the maximum, the vapor does not follow Boyle's law nor Gay Lussac's temperature law; but as the temperature at constant pressure rises, or as the pressure at constant temperature diminishes, the vapor tends to obey these laws more and more, and finally the deviation becomes negligible. That is, when the intensity of the heat energy is not relatively high, the intensity of volume energy is inversely proportional to the capacity only when the intensity of the volume energy

is low; when, however, the intensity of the heat energy is relatively high, then the intensity of the volume energy may also be high, and the two factors of the volume energy still vary in inverse proportion. Oxygen, hydrogen, nitrogen, methane, nitrous oxid, helium, argon, and a few other gases represent such collections of energy that the ordinary temperature is a sufficiently high intensity to admit of the inverse relations between the factors of the volume energies for moderate values of the intensity factor, pressure.

We shall find it convenient to distinguish between vapors and gases. We shall call a *vapor* an aëriform collection of energies in which the factors of the volume energy do not obey Boyle's law; a *gas*, a collection in which the factors do obey Boyle's law. This is in harmony with the distinction made in § 24. There is another distinction to be considered later.

Let us apply equation 19 to a vapor at constant temperature. It becomes

$$dQ = \frac{\partial U}{\partial v} dv + p dv. \qquad 25$$

Consequently the heat is partially or completely changed into external work according to whether the internal energy changes with the volume or not. We can settle this experimentally in the following way.

32. **Internal energy of a gas.** — Imagine a gas under moderate pressure in a vessel which communicates with another vessel by a tube and tap. The second vessel is well evacuated. This system is placed in a calorimeter. On opening the tap, the gas passes into the evacuated vessel until the pressure in each vessel is equal. The volume changes under such conditions that any gain or loss of energy causes a change in the temperature of the calorimeter. When the gas is either oxygen, hydrogen, or nitrogen, or one of the few other gases cited above, the change in temperature is extremely small, but with all other

gases the change in temperature is very marked. So that the internal energy may be considered practically independent of the volume only in the first set of gases, and it is not perfectly independent for any gas so far known. This is consistent with the slight variation in specific heat at constant volume at different temperatures.

In a perfect gas the internal energy is perfectly independent of the volume.

In this case $\partial U/\partial v = 0$, and 25 becomes

$$dQ = pdv = RT\frac{dv}{v}; \qquad 26$$

that is, at constant temperature all the heat energy, passing into a perfect gas, changes into volume energy on its way into mechanical energy or its equivalent. This gives us another definition for a perfect gas; namely, a perfect gas is a collection of such energies that heat energy can be completely changed into volume energy.

33. **Mechanical equivalent of heat.**—With this understanding, we can proceed to determine the mechanical equivalent of heat; that is, to determine the quantity of linear energy, either in gravity energy or in absolute units of work, that one calorie equals.

The difference between the molecular heats of a perfect gas under constant pressure and at constant volume is due to the external work done by the gas when under constant pressure. We cannot get perfect gases, but for this particular purpose atmospheric air is perfect enough. As air is a mixture, we consider one gram instead of a grammolecule.

The specific heat of air at constant volume is 0.1683 cals.; under constant pressure it is 0.2375 cals. A gram of air at 76 cm. pressure and 0° C. temperature occupies 773.3 cc. When heated one degree, it expands $773.3\frac{1}{273} = 2.83$ cc. against a pressure of 76 cm. of mercury. The volume energy corresponding to this is $76 \cdot 13.6 \cdot 2.83 = 2965.1$ linear energy units

measured in gravity units. To get this quantity of energy, $0.2375 - 0.1683 = 0.0692$ cals. were required. So

$$1 \text{ cal.} = \frac{2965.1}{0.0692} = 42848 \text{ gravity units of work.}$$

A number of very accurate experiments have been made in different ways to determine the mechanical equivalent of heat. They have led to the mean value 42750 gravity units.

$$42750 \text{ gravity units} = 42750 \cdot 981 = 41937750 \text{ ergs.}$$

34. **Difference between molecular heats under constant pressure and at constant volume.** — This difference is the same for one grammolecule of any gas whose internal energy does not change with the volume. One grammolecule occupies $2/0.0_49 = 22222$ cc.; so, when heated one degree, it expands $22222 \cdot 1/273$ cc., and the external work done when expanding against p_0 is $(22222/273)76 \cdot 13.6 = 84110$ gravity units $= 84110 \cdot 981 = 82510000$ ergs. This is the work equivalent to the difference between the molecular heats under constant pressure and at constant volume. Referring to § 21, we see it is equal to R; so

$$C_p - C_v = R = 2 \text{ cals.} \qquad 27$$

35. **Available energy from the expansion of a gas; no heat supplied from without.** — Equation 13 gives the available energy from the expansion of a gas when heat is supplied from without to keep the temperature constant, and equation 26 tells us all this heat is changed into volume energy and then into linear energy or work.

We are now to consider the case in which no heat is supplied to the expanding gas. A change which takes place when no heat is supplied is called an *adiabatic* change.

In an adiabatic change the temperature changes. If the change be an expansion, the mechanical work is made up from the heat energy in the gas, and so the temperature falls. If

the adiabatic change be a compression, the temperature evidently rises.

The equation suitable for this case is 19. We have seen that for fairly perfect gases $\partial U/\partial v = 0$, also $\partial U/\partial T = C_v$, and as no heat is to be added, $dQ = 0$; so 19 reduces to

$$0 = C_v dT + p dv. \qquad 28$$

As we are to get the available energy, we must eliminate dT. This may be done by differentiating 10, giving

$$RdT = p dv + v dp, \qquad 29$$

which, on combining with 28, gives

$$0 = (C_v + R) p dv + C_v v dp.$$

With 27, $$0 = C_p p dv + C_v v dp.$$

Rearranging, $$0 = \frac{C_p}{C_v}\frac{dv}{v} + \frac{dp}{p}.$$

Integrating between the limits of the expansion, p_0, v_0, p_1, v_1,

$$\frac{C_p}{C_v} l\frac{v_0}{v_1} = l\frac{p_1}{p_0}.$$

The ratio C_p/C_v is important and often used, so it is well to denote it by a symbol K. So the equation can be written

$$\left(\frac{v_0}{v_1}\right)^K = \frac{p_1}{p_0}. \qquad 30$$

This equation gives the relation between pressure and volume when the gas expands adiabatically. Let p_0, v_0 be the initial pressure and volume, respectively; from equation 12, remembering that the value of p in terms of v must now be taken from 30, we have

$$\int_{W_0}^{W_1} dW = p_0 (v_0)^K \int_{v_0}^{v_1} \frac{dv}{v_1^K};$$

hence $$W = W_1 - W_0 = \frac{p_0 (v_0)^K}{1 - K}\{v_1^{1-K} - v_0^{1-K}\}, \qquad 31$$

which gives the available work when a gas expands adiabatically. The reader must remember that 28 is only strictly true for a perfect gas.

If, instead of substituting dT from 29 in 28, we substitute pdv, we get

$$0 = (C_v + R)\,dT - v\,dp.$$

Combining with 10 and 27,

$$\frac{dp}{p} = \frac{C_p}{C_p - C_v}\frac{dT}{T} = \frac{K}{K-1}\frac{dT}{T}.$$

Integrating between the limits p_0, p_1, T_0, T_1,

$$l\frac{p_1}{p_0} = \frac{K}{K-l}\,l\frac{T_1}{T_0},$$

or

$$\frac{p_1}{p_0} = \left(\frac{T_1}{T_0}\right)^{\frac{K}{K-1}}. \qquad 32$$

Combining with 30,

$$\frac{v_0}{v_1} = \left(\frac{T_1}{T_0}\right)^{\frac{1}{K-1}}. \qquad 33$$

Equation 31 can be simplified by combining with 33 and 10. The right-hand member of 31 becomes

$$\frac{1}{1-K}\left[p_0 v_0 \left(\frac{v_0}{v_1}\right)^{K-1} - p_0 v_0\right] = \frac{R}{1-K}(T_1 - T_0),$$

and so

$$W = \frac{R}{1-K}(T_1 - T_0). \qquad 34$$

36. **The second law of thermodynamics.** — Equation 26 states that all the heat put into a perfect gas can pass through volume energy into work, but it does not state that when we have a quantity of heat energy it will be possible to put all that energy into a gas and so change it into work.

We shall now proceed to determine how much of a given quantity of heat energy can be changed into work. The ex-

pression of this ratio forms the second law of thermodynamics.

The simplest way to determine this is to let a gas pass through a series of changes which involve only heat energy and linear energy, the two being connected through volume energy. As a gas is a collection of forms of energy, it would be very possible for the internal energy of the gas to supply some of the linear energy, or for some of the heat to stay in the gas as internal energy, did we not make the gas which is used finally return to its initial state. We make the gas pass through a *cycle* of changes. A *cycle of changes is a series of changes such that the final and initial states are identical.* Then, if the internal energy of the gas changes in any operation, that change is balanced in some other operation, for the internal energy of a body is determined only by the state it is in, not by the manner in which it reaches that state. This is a matter of experimental knowledge. So as the final and initial states of the gas are identical, the internal energy of the gas is the same at the end as at the beginning. To make sure that no energy has leaked away while changing into the desired energy, or that some energy has not crept in from without the system, we select such a cycle that we can reverse the order of operations, and then if everything goes right, the linear energy obtained suffices to quantitatively reproduce the heat energy lost; we use a *reversible* cycle. In a *reversible cycle the energy obtained at the end of the cycle is just equal to the energy consumed.* There is neither a leakage nor a gain of energy. In a *non-reversible cycle or a natural cycle there is either a leakage or a gain of energy.* This an ideal arrangement. There are no reversible cycles in nature, but the conclusions we reach through a reversible cycle are nevertheless of great importance. They are the results of perfect action, and on comparison with actions such as we find in nature, lead to the detection of the causes of imperfection.

The engine needed is a cylinder containing a fixed quantity

of a perfect gas and a piston sliding in the cylinder without any friction, and, of course, perfectly tight. The quantity of gas may be what we choose, but it must not change during the cycle of changes. We also need two reservoirs of heat at T_1 and T_2 temperature. These reservoirs must contain so much heat that the removal of the quantity needed in heating the gas, or the addition of the quantity rejected on cooling the gas, will make no appreciable alteration in the temperature of the reservoirs.

(1) Start with the gas in the cylinder and piston pressing on the gas with pressure p_1, volume is v_1, and temperature T_1. The cylinder is put into the reservoir at T_1 and the gas allowed to expand, the external pressure being kept at a pressure just less than the pressure of the gas. The total quantity of heat taken up is

$$Q_1 = RT_1 l \frac{v_2}{v_1}. \qquad 35$$

(2) The cylinder is then taken out and the gas allowed to expand adiabatically until its temperature is T_2. Its volume is then v_3. The relation between volume and temperature is given by 33; namely,

$$\frac{T_1}{T_2} = \left(\frac{v_3}{v_2}\right)^{K-1}. \qquad 36$$

(3) The cylinder and gas, now at T_2, is put into the reservoir at T_2 and the gas compressed to volume v_4 such that the succeeding adiabatic compression can diminish the volume to v_1 and raise the temperature to T_1. The heat of the isothermal compression is

$$Q_2 = RT_2 l \frac{v_3}{v_4}. \qquad 37$$

(4) In the succeeding adiabatic compression, which completes the cycle, we have

$$\frac{T_1}{T_2} = \left(\frac{v_4}{v_1}\right)^{K-1}. \qquad 38$$

We see from 36 and 38 that

$$\frac{v_3}{v_2}=\frac{v_4}{v_1},$$

or

$$\frac{v_3}{v_4}=\frac{v_2}{v_1}. \qquad 39$$

From 35, 37, and 39,

$$\frac{Q_1}{Q_2}=\frac{T_1}{T_2}\frac{l\frac{v_2}{v_1}}{l\frac{v_3}{v_4}}=\frac{T_1}{T_2}, \qquad 40$$

or

$$Q_1-Q_2=Q=W=Q_1\frac{T_1-T_2}{T_1}, \qquad 41$$

where W is the work obtainable from Q_1. When the change in temperature is very small,

$$dW=Q\frac{dT}{T}. \qquad 42$$

The first member of 41 is the difference between the heat put into the gas and the heat taken out; it is therefore the heat changed into work. T_1-T_2 is the range of temperature through which the engine runs while Q_1-Q_2 is changed into work. As $T_2<T_1$, the range of temperature is a descent.

Equations 41 *and* 42 *are the analytical expressions of the second law of thermodynamics as applied to a simple system.*

Equation 41 states that the quantity of available linear energy is directly proportional to the descent in temperature in the engine, and inversely proportional to the temperature at which the original heat energy passes into the engine.

We have deduced the relation between W and Q in a particular way, but the result must be the same whatever way we follow, provided, of course, Q_1, Q_2, T_1, T_2 are the same. For if not, we take the cycle which yields the larger quantity of work, and with this work run the other cycle backward to the initial state. The result is that a reversible cycle which

yields a certain quantity of work, on reversal, is able to assimilate a larger quantity of work than it yields and yet be in the same final state after each operation. This means a destruction of energy. So 41 or 42 must be true for every engine.

Let us in the future give the minus sign to energy when it is lost by the system, and the plus sign to energy when it is gained by the system. We can then write

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}=0. \qquad 43$$

This is another analytical expression of the second law of thermodynamics as applied to a simple system.

We may apply the same deduction to any cycle however complicated, for we can resolve it into a large number of small cycles for each of which equation 43 will be true. When the complicated cycle is such that T varies with Q, then we make Q so small that T may be considered constant, and we get

$$\int\frac{dQ}{T}=0, \qquad 44$$

which is the general analytical expression of the second law of thermodynamics.

As there are no strictly reversible cycles in nature, 44 must be somewhat changed when applied to natural occurrences. When we examine the conditions that admit of a passage of heat, we find that the temperature of the supplying body is always somewhat higher than the temperature of the receiving body; that is, the temperature of the heat received is somewhat higher than its temperature in a natural cycle for the same quantity of heat, and the quantity of heat rejected is a little more in a natural cycle than it is in a reversible one for the same range of temperature. So the plus terms of 44 are a little smaller in a cycle of nature than in a reversible one, and

the negative terms are a little larger in a natural cycle than in a reversible one. The result is that in a natural cycle

$$\int \frac{dQ}{T} < 0. \qquad 45$$

Since equation 44 is true for all reversible cycles, the differential is perfectly definite, and we may put

$$\frac{dQ}{T} = dS. \qquad 46$$

The quantity S is called the *entropy*. When dQ is zero, dS is likewise zero, so adiabatic changes are often called *isentropic* changes.

37. **Change of internal energy with the temperature.** — Let Q be the heat involved in changing one substance into another at constant pressure; then Q is the change of internal energy, U, of the first body when it passes into the second body. We are to determine $dQ/dT = dU/dT$.

(1) Let one grammolecule of A change into B at T; change of internal energy $= \pm Q = \pm U$.

(2) Heat B to $T + dT$; change in internal energy $= + C_2 dT$, where C_2 is the molecular heat of B.

(3) Change B back into A at $T + dT$; change of internal energy $= \mp (Q + dQ) = \mp (U + dU)$.

(4) Cool A to T; change of internal energy $= - C_1 dT$, where C_1 is the molecular heat of A.

This completes the cycle, which is reversible, so

$$\pm U + C_2 dT \mp U \mp dU - C_1 dT = 0,$$

or

$$\frac{dU}{dT} = \frac{dQ}{dT} = C_2 - C_1. \qquad 47$$

That is, *the heat of transformation increases with the temperature when the molecular heat of the product is greater than that of the initial body*, but *the heat of transformation decreases as the*

temperature increases where the molecular heat of the product is less than that of the initial body.

When the change is a vaporization, as C_1 is always greater than C_2, the heat of vaporization always decreases as the temperature rises.

CHAPTER IV.

PHYSICAL CHANGES.

38. **Physical changes.** — We now proceed to apply the two preceding laws; more particularly the second, for the application of the first is very simple.

The second law is to be used whenever heat energy and linear energy or work, or its equivalent, are involved. As heat energy is involved in most changes, the second law is of very wide application.

In this chapter we shall consider some very important *physical* changes. A *physical change* is a change which does not alter the characteristic chemical nature of the body.

39. **Fusion.** — Let v''' be the volume of a grammolecule of a solid, v'' that of the same quantity of the liquid. Supposing that the solid expands on melting, let p be the pressure on the solid, just sufficient to prevent it from melting at T.

The differential of work, dW, in 42, becomes

$$dW = pdv = vdp = (v'' - v''')\,dp,$$

where $v'' - v'''$ is the change in volume on melting. So, from 42

$$Q = T(v'' - v''')\frac{dp}{dT}, \qquad 48$$

where T is the absolute temperature of the change, that is, the absolute fusion temperature, dp/dT, the change in fusion pressure with the temperature, and Q, the molecular heat of fusion. Since Q is always positive, $v'' - v'''$ and dp/dT must have the same signs so that when a body expands on melting, a rise in fusion temperature requires a rise in fusion pressure; when a

body contracts on melting, a rise in fusion temperature requires a decrease in fusion pressure.

Problems.

1. For ice under 76 cm. pressure, $v''' = 19.62$ cc., $v'' = 18.00$ cc., $Q = 1433$ cals., $T = 273$. What change in pressure is needed to lower the fusion temperature 1°?

Ans. $134 \cdot 76$ cm. Hg $= 134$ atms.

2. For acetic acid $v'' - v''' = +9.57$ cc., fusion temperature $= 16.6°$ C., under 76 cm. Hg, $dT/dp = 0.0242°$. What is the molecular heat of fusion? *Ans.* 2763 cals.

Pressure does not seem to affect solids and liquids to the same extent, so for a certain pressure and corresponding temperature we may expect to find $v'' = v'''$ unless the body decomposes before reaching the fusion temperature. In that case, from 48,

$$Q\frac{dT}{dp} = T(v'' - v''') = 0,$$

so that unless $Q = 0$, we have $dp/dT = 0$; that is, at the particular pressure at which there is no change in volume when the solid melts, and Q does not $= 0$, a change in pressure does not change the melting point.

At a higher pressure, $v'' - v'''$ changes sign, and unless Q is negative, dT/dp likewise changes sign. In this case, where $Q > 0$, a change in pressure has an opposite effect to what it had before the pressure reached the value that made $v'' = v'''$.

Such cases are known. They seem to correspond to the critical cases for vapors.

3. The same principle may be applied to change in crystalline form. The heat absorbed when 1 grammolecule rhombic sulfur passes into monoclinic sulfur is 81 cals.,

$$v_2''' - v_1''' = 0.403 \text{ cc.},$$

where v_1''' = volume of one grammolecule rhombic sulfur, v_2''' that of monoclinic sulfur. What is the change in temperature of transformation for an increase in pressure of 100 cm. Hg? The temperature at which rhombic sulfur under 76 cm. Hg changes into monoclinic sulfur is 95.6° C. *Ans.* 0.058°.

40. **Sublimation.** — We define sublimation as the change of a solid directly into a vapor without first melting. The word commonly implies a change back into the solid state; we shall not use it in that sense.

Here v'' of 48 becomes v', the molecular volume of the vapor, and

$$Q = T(v' - v''')\frac{dp}{dT} = Tv'\frac{dp}{dT}, \qquad 49$$

when v''' is negligible in comparison with v'.

When it is possible to adjust pressure and temperature so that

$$v' \gtrless v''', \text{ then } \frac{dp}{dT} \gtrless 0,$$

provided $Q > 0$.

When $v' = v'''$, then unless $T = 0$, and $Q \gtrless 0$, $dp/dT = 0$.

41. **Vaporization.** — In this case 48 becomes

$$Q = T(v' - v'')\frac{dp}{dT}, \qquad 50$$

or

$$Q = Tv'\frac{dp}{dT}, \qquad 51$$

when v'', the molecular volume of the liquid, is negligible in comparison with v'.

When p is low, the vapor may be supposed to obey the gas law. In that case, dropping the dash, 51 becomes

$$Q = \frac{RT^2}{p} \cdot \frac{dp}{dT} = RT^2\frac{dlp}{dT}. \qquad 52$$

Problems.

1. For water at 99° C., $p=73.33$ cm. Hg; at 100° C., $p=76.00$ cm. Hg; at 101° C., $p=78.76$ cm. Hg; v' at 100° C. $=29844$ cc.; $v''=18$ cc. What is the molecular heat of vaporization?

Ans. 9596 cals.

2. The boiling point of benzene at 74.2 cm. Hg is 79° C.; for change in pressure = 2.9 cm. Hg, change in boiling point = 1.28° C. What is the molecular heat of vaporization of benzene?

Ans. 7565 cals.

3. The boiling point of ethyl iodid at 73.3 cm. Hg is 72.2° C.; $Q=7597$ cals. What is the change in vapor pressure for 1° C.?

Ans. 2.34 cm. Hg.

Let Q_1 be the molecular heat of fusion, and Q_2 the molecular heat of vaporization of a melted body at its fusion temperature. Then from 48 and 50,

$$Q_1+Q_2=Q_3=T\left\{(v''-v''')\frac{dp_1}{dT}+(v'-v'')\frac{pd_2}{dT}\right\}, \qquad 53$$

where Q_3 is the molecular heat of sublimation, p_1 the fusion pressure, and p_2 the vapor pressure. This equation is useful in determining molecular heat of sublimation. Also

$$Q_1=Q_3-Q_2=Tv'\left(\frac{dp_3}{dT}-\frac{dp_2}{dT}\right), \qquad 54$$

where p_3 is the sublimation pressure.

The relations between pressure and temperature for a solid and for a liquid come out very plainly on plotting curves in which p is the ordinate and T the abscissa.

Let AB connect p and T. At A, the liquid freezes, and the relation between these two variables is ready to change abruptly. If the liquid did not freeze, the relation between p and T would not change abruptly, but would be something like the dotted line AO running to absolute zero. A part of

AO has been followed experimentally under such conditions that the liquid did not freeze.

After the liquid has frozen, the relation between p and T is shown by AC. Below C we have the dotted continuation CO, which has not been followed experimentally. If the solid did

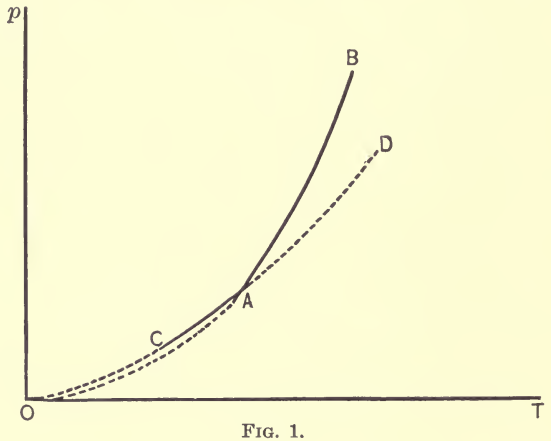

FIG. 1.

not melt at A, we should get the curve AD. A part of this has been followed experimentally under such conditions that the solid did not melt.

The vapor pressure of any solid is the same as that of the liquid at the temperature at which they coexist. For imagine the annular vessel of Fig. 2 to contain on one side liquid and on the other side solid, both in contact at the lower part of the ring. Were the vapor pressure of the water not equal to the vapor pressure of the ice, vapor would pass from one side to the other; so that one of the substances, say the ice, would be constantly formed at the top, owing to the increased pressure on its vapor and consequent condensation. Heat would therefore be given off on the side of the solid as it increased, while heat would be absorbed by the vaporizing liquid. This would

be a perpetual absorption of heat and production again without a sufficient cause. So ice and water at 0° C., or at any other temperature at which they coexist, must be considered to have equal vapor tension.

The reader will notice that the curve for ice suddenly changes as it passes into that for water. There is a singular

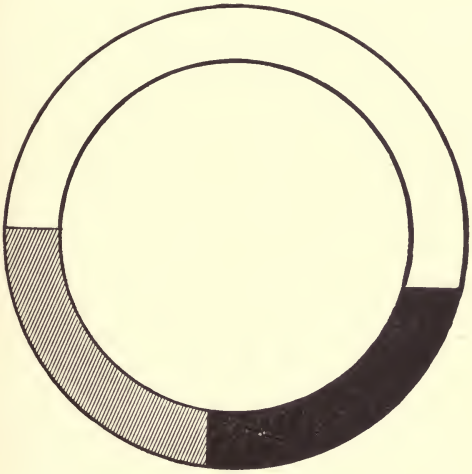

Fig. 2.

point at the place where they coexist. Conversely, when we plot a curve for any substance, relating two forms of energy or their factors, and find a singular point, we have a right to say that as this position marks a change in the relations of the energies, it therefore marks the formation of a new substance.

42. **Solutions.** — A solution is a homogeneous mixture of two or more substances. We say a mixture is homogeneous when the evidence of our senses, with some instrumental aid at times, will not show any difference in composition in different parts of the mixture.

The term is somewhat vague, for we cannot say just how much instrumental aid is allowable. An emulsion of oil and water is not a solution, for the microscope will distinguish particles of oil from particles of water. Sugar dissolved in water is a solution, though a dialyzer will partially separate sugar from water.

The only bodies we should call strictly homogeneous are the elements; in a somewhat loose way all chemical compounds are homogeneous; much more loosely we call solutions homogeneous. The latter pass, with diminishing homogeneity, through colloid solutions into emulsions.

We shall call the body which is present in largest proportion the solvent, the other body or bodies in the liquid mixture the solute or solutes.

43. **Gaseous solution.** — These are the simplest solutions possible. When the intensity of the volume energy, p, is low, the properties of the mixture are the sum of the properties of the constituents; when the intensity is high, the properties of each constituent are more or less modified. Solutions of liquids and of solids in gases are said to exist. Solids seem to volatilize more readily in the presence of some other vapor or gas than when this gas or vapor is absent. So some chemists claim that the solid dissolves in the vapor or gas. It would be better to say that this is simply the solution of a vapor in a vapor or gas, the phenomenon being apparently like solution in a liquid, due consideration being taken of the greater volume energy possible in a liquid. It is misleading to speak of a solid dissolving in a vapor or gas, as that implies the presence of the solid as such in the vapor or gas, which is not the case of all.

44. **Solid solutions.** — A homogeneous mixture of two solids is a solid solution. Comparatively little is known about them. Substances which crystallize in indefinite proportion, so called mixed crystals or composite crystals, are examples.

Solutions of gases in solids are also known, but not enough about them to warrant consideration here.

A few solutions of liquids in solids are known.

45. **Liquid solutions.** — These are by far the most numerous. Their properties are generally different from the sum of the properties of the constituents.

46. **Henry's law.** — We shall claim that all liquids dissolve all gases. In a few cases, the quantity of gas dissolved is so small that it cannot always be detected by chemical means, but analogy justifies us in claiming that some gas is always dissolved. Such liquids as mercury and sulfuric acid dissolve but inappreciable quantities of gases. Other liquids sometimes dissolve so much gas or vapor that a chemical combination is suggested, — for instance, aqueous solutions of ammonia and hydrochloric acid, — but the physical properties of these solutions show that they are not chemical compounds.

Leaving these extreme cases out of account, provided the molecular weight of the gas or vapor as such and in solution are the same, we find that at constant temperature *the mass of gas dissolved by a fixed mass of liquid is directly proportional to the pressure on the gas.* This is *Henry's law.* When the molecular weights in aëriform state and in solution are not the same, the law must be applied to each set of molecules separately. We shall see later how to do this. We may state the law in volume instead of pressure: *at constant temperature a given mass of liquid dissolves the same volume of gas whatever the pressure may be.* We may also say that *the ratio of the concentration of the gas or vapor in the gaseous space to its concentration in the liquid is constant.* Here concentration is *volume concentration;* namely, *the mass in unit volume.*

The volume of gas, measured at 0° and 76 cm. Hg, dissolved by a unit volume of liquid measured at 0° C. and 76 cm. Hg, is called the *coefficient of absorption* of the gas, and is denoted by α.

The ratio of volume of gas dissolved to volume of liquid, both at the same temperature and pressure, which may be any

temperature and pressure, is called the *solubility* of the gas, and denoted by s; so

$$s = \frac{v'}{v''}, \qquad 55$$

where v', v'' are respectively volume of gas and of liquid.

The coefficients of absorption seem to diminish as temperature increases; no coefficient is positively known to increase with temperature, though hydrogen sulfid would seem to dissolve in melted sulfur in quantities increasing with the temperature.

As to the state of the gas in solution, it would seem as if it were in the same state as the liquid. This will appear from reasons given hereafter. (See § 58.)

In applying Henry's law to a mixture of gases, each constituent is to be treated separately.

47. **Liquids in liquids.** — We shall claim that all liquids give off vapor, and as all vapors are soluble in all liquids, it follows that all liquids are soluble in each other. But whereas gases and vapors are always soluble in each other, under all conditions in all proportions, liquids are not always soluble in each other under all conditions in all proportions. For instance, on shaking up equal volumes of water and ether, the mixture separates, on standing, into two layers, the lower containing about 10% ether in 90% water, the upper about 3% water in 97% ether.

When, however, the temperature of such a mixture is raised, and the pressure increased sufficiently, at a certain temperature the two layers usually merge into one, and above this temperature the two liquids are soluble in each other in all proportions. The temperature at which two liquids become soluble in each other in all proportions is sometimes called the *critical temperature of solution*.

On the other hand, it sometimes happens that a solution of one liquid, soluble in another in all proportions, separates on rise of temperature into two layers.

Some solids which dissolve easily in a particular solvent

seem to have also a critical temperature of solution above which they dissolve in all proportions in that particular solvent.

So we may state that theoretically all liquids can be made to dissolve in each other in all proportions under certain conditions, not under all conditions, and probably the same may be stated of the solubility of solids in liquids.

48. **Vapor pressure of solutions.** — The vaporization of a gas from a solid solution is to be treated in the same way as the vaporization of a vapor or gas from a liquid solution. We pass right on to liquid solutions.

When the substance in solution does not give off an appreciable quantity of vapor, the vaporization is very simple; but since all liquids give off vapor, and since all substances in solution seem to be liquids, we shall claim that all substances in solution give off some vapor, though the quantity may be too small to detect. We shall return to such solutions later.

The vaporization of a solution of liquids is more complex; we must be content with the general aspects of the case.

Consider two liquids at some convenient temperature which dissolve in each other in all proportions, say A and B (Fig. 3). Let the vapor pressure of pure A be given by the first vertical of figure 3; that of pure B, by the second vertical. Let the percentage of B in A be given by the abscissa, and the vapor pressure by the corresponding ordinate. We have the following cases. The curves are essentially qualitative only.

(1) The addition of a small quantity of B to A gives a solution having smaller vapor pressure than A; A has the same effect on B. We get curve I.; example, water and formic acid.

(2) The addition of a small quantity of B to A has the same effect as in No. 1, but the addition of A to B gives a solution of higher vapor pressure than B. We get curves II., III., or IV. according to whether A or B has the higher vapor pressure. Curve II. represents water and methyl alcohol; curve III., water and ethyl alcohol; curve IV. is theoretical.

(3) The addition of a small quantity of B to A and A to B has the effect of A to B in (2). We get curve V.; example, water and propyl alcohol.

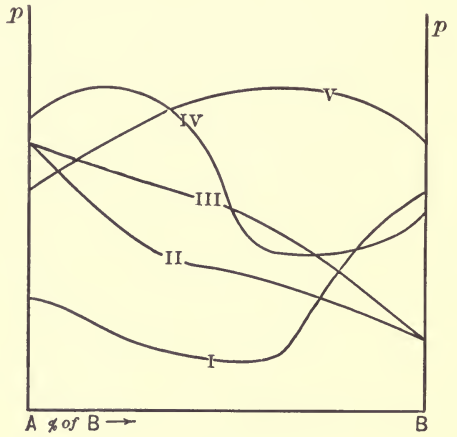

FIG. 3.

In a general way the preceding cases cover all solutions containing only two substances; when there are more than two, the matter is more complicated.

49. **Fractional distillation.** — Since the vapor pressure of a solution changes with the concentration, it is generally possible to make a more or less complete separation of the constituents.

Let us heat a solution that has a vapor curve like III., and suppose we start with a 50 % solution of B in A. The temperature of the solution rises until its vapor pressure equals the external pressure, when the liquid boils. Let us remove the vapor as fast as it forms. We see from the curve that a liquid consisting of pure A has the highest vapor pressure possible, but the vapor cannot consist of pure A since B also gives off vapor. Yet it is very evident that the vapor will be richer in A than the solution at that temperature, so that on condensing the vapor we shall obtain a liquid richer in A than the original

solution. As A passes off, the vapor pressure of the solution diminishes; consequently to keep its pressure up to the external pressure its temperature has to be raised. As A passes off, the solution in the still becomes more and more concentrated in respect to B, and consequently the percentage of B in the vapor increases continually. When the distillate begins to get too rich in B, the distillation is stopped or the receiver changed as often as seems proper, say after each rise of 5° in boiling point. On repeating the distillation with the distillates often enough, we can get A and B pure enough. This is *fractional distillation.*

Let us distil a solution belonging to curve I. containing 40 % B in A, and suppose the minimum vapor pressure is at 60 % B in A. Then, as A passes off more rapidly than B, the solution concentrates in respect to B until it reaches 60 % B; then it cannot concentrate any further, for a liquid containing a little more B than the liquid in the still has as high a vapor tension as a liquid containing a little more A than the liquid in the still. Therefore the composition of this part of the solution is not changed by further distillation. The distillate, richer in A than the original liquid, is repeatedly distilled, and if we distil often enough, we shall get A pure enough; but no liquid containing more than 60 % B can be obtained by fractional distillation from the 40 % solution.

Problems.

1. Distil a solution following curve I. and containing 75 % B. What is the best separation you can make?

2. Answer the same question for solutions following respectively curves II., IV., V.

In the case of a system composed of two liquids not soluble in each other in all proportions at the temperature of distillation, as water and ether, we have two solutions, and each solution is to be treated by itself.

Two solutions in equilibrium with each other have the same vapor pressure. This is seen on referring to Fig. 2 and imagining the solution of A in B on one side, and the solution of B in A on the other. If one solution has a higher vapor pressure than the other, that solution commences to distil into the solution of lower vapor pressure which disturbs the equilibrium at the boundary of the liquids. These adjust themselves again to restore the portion of liquid of higher vapor pressure which distilled over, and so the operation continues for an unlimited time and gives an unlimited quantity of work without a corresponding consumption of heat. This is impossible, and so the vapor pressure of solution of A in B equals the vapor pressure of solution of B in A. It follows from this that, at constant temperature, a curve showing the vapor pressure of a solution of B in A must intersect a similar curve for A in B, where A is saturated with B, and that at this point B must also be saturated with A.

In such cases the curve showing relation of vapor pressure to composition is like Fig. 4, though c may often coincide with d. The ordinate gives the vapor pressure; the abscissa, the percentage of B in A.

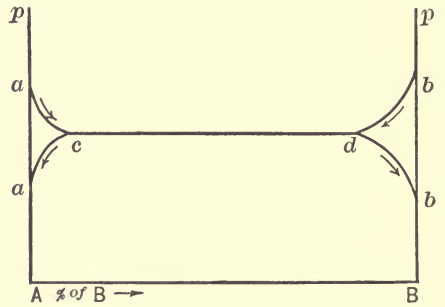

Fig. 4.

Suppose we distil a solution of B in A, not enough B in A to saturate A with it. Suppose A has the higher vapor

pressure, and therefore passes off more rapidly than B, so that the curve is something like ac. But a time will come when, on continuing distillation, A finally becomes saturated with B. As A continues to pass off, a second liquid appears consisting of B saturated with A, having a vapor pressure equal to that of A saturated with B at that temperature. As we continue the distillation, the vapor does not change until one of the solutions disappears, the other solution supplying the necessary bodies. This part of the curve is the horizontal, cd. Finally the quantity of A is so reduced that it can no longer form a solution of B in A, and the horizontal line passes into the curve of a solution of A in B, db. When B has the higher vapor pressure, the curve runs from right to left.

Two liquids not soluble at all in each other cannot have any effect on each other, and so the vapor pressure of the mixture must be the sum of the vapor pressure of each constituent. This is an ideal case, though there are some liquids which very closely approach it.

When the system consists of a gas and one or more liquids giving off vapor, *the pressure of the whole system equals the pressure of the gas plus the sum of the vapor pressures of the liquids.* This is *Dalton's law of partial pressures.* It is not strictly true, as there are no liquids which do not partially dissolve the gas, and a secondary effect is hereby produced, but Dalton's law is accurate enough for many purposes.

50. **Surface energy.** — The most characteristic energy in the collection of energies forming a liquid is surface energy. It is an energy found on the surface of all liquids, and acts so as to make the surface of liquids as small as possible. It is probably on account of the surface energy that liquids have a definite volume.

The intensity of surface energy is surface tension, its capacity is surface. The analytical expression of surface energy S is

$$S = \gamma s,$$

where γ is the surface tension and s the surface. The surface tension is independent of the surface. It is dependent on the temperature.

Surface tension is generally defined as the force in gravity, units, or in dynes, acting on the length of 1 cm. of surface of liquid. It is determined in several ways. The simplest in principle is this.

A tube of very small bore and scrupulously clean, open at each end, is supported vertically in the liquid whose surface tension is to be determined. If the liquid wets the tube, it will creep up the inside, and some liquid is drawn up, for the surface of the liquid inside the tube is thereby diminished. The surface of the liquid will make an angle θ (sometimes $= 0°$), and the tension balancing the gravity force is the vertical component (see A, Fig. 5). So if γ is the tension, the vertical component is $\gamma \cos\theta$, the length of its action is $2\pi r$; so the surface that diminishes is $2\pi r dh$, where dh is the change in height of the column of liquid, and the change in surface energy is $\gamma \cos\theta\, 2\pi r dh$. This is balanced at equilibrium by the change in gravity energy. The mass of liquid is $\pi r^2 \sigma h$, where σ is the density of the liquid and h the height of the column of liquid; the change in gravity energy is $\pi r^2 \sigma h dh$, so

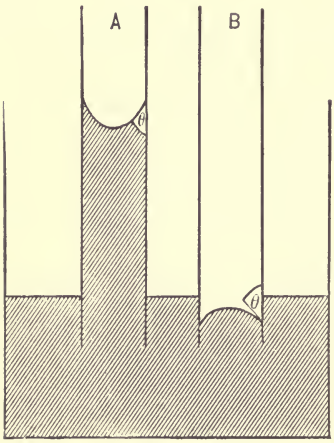

FIG. 5.

$$\gamma \cos\theta\, 2\pi r dh = \pi r^2 \sigma h dh,$$

or

$$\gamma = \frac{r\sigma h}{2\cos\theta}. \qquad 56$$

When the liquid does not wet the tube, h is measured downwards (see B, Fig. 5).

Since solids crystallize from liquids, and as there is a surface tension at the surface dividing solid and liquid, we are led to the idea of a surface tension of a solid. We cannot go into this, however.

51. **Determination of molecular weights of liquids.** — (1) Consider a grammolecule each of two liquids and their saturated vapors at *corresponding* pressures and temperatures. We see from equation 17 that then $\phi_1'' = \phi_2''$ and $\phi_1' = \phi_2'$, where ϕ_1'', ϕ_2'', ϕ_1', ϕ_2', are the *corresponding* volumes of the two liquids and vapors respectively. By definition,

$$\phi_1' = \frac{v_1'}{\phi_0'}, \quad \phi_2' = \frac{v_2'}{\phi_0''}, \quad \phi_1'' = \frac{v_1''}{\phi_0'}, \quad \phi_2'' = \frac{v_2''}{\phi_0''},$$

where v_1', v_2', v_1'', v_2'', are the molecular volumes of the two vapors and liquids and ϕ_0' and ϕ_0'' are the critical volumes of the two liquids. The student will remember that there is only one critical volume for each substance. Hence,

$$\frac{v_1''}{v_1'} = \frac{v_2''}{v_2'}.$$

Replacing v_1' and v_2' from the gas equation, $pv = RT$, and therefore assuming that these vapors behave as gases, we get

$$\frac{p_1' v_1''}{T_1} = \frac{p_2' v_2''}{T_2}. \qquad 57$$

As v_1'' and v_2'' are the volumes of a grammolecule each, the surfaces of the grammolecules are $(v_1'')^{\frac{2}{3}}$ and $(v_2'')^{\frac{2}{3}}$, and the pressures on these two surfaces are $p_1'(v_1'')^{\frac{2}{3}}$ and $p_2'(v_2'')^{\frac{2}{3}}$.

The length of one side of the grammolecules when in the shape of cubes are $(v_1'')^{\frac{1}{3}}$ and $(v_2'')^{\frac{1}{3}}$, and the surface tension along such sides is $\gamma_1(v_1'')^{\frac{1}{3}}$, and $\gamma_2(v_2'')^{\frac{1}{3}}$.

Now experiment seems to justify the claim that when bodies are in corresponding states in the sense of equation 17, that is

in regard to vapor and liquid, they are so in regard to many other physical properties. Therefore we may put

$$\frac{\gamma_1}{p_1'(v_1'')^{\frac{1}{3}}} = \frac{\gamma_2}{p_1'(v_2'')^{\frac{1}{3}}}. \qquad 58$$

From 57 and 58 we get

$$\frac{\gamma_1'(v_1'')^{\frac{2}{3}}}{T_1} = \frac{\gamma_2(v_2'')^{\frac{2}{3}}}{T_2}. \qquad 59$$

From the definition of corresponding temperatures and from the remarks just preceding equation 58, we see that 59 is true at any two temperatures, provided only that the temperatures are in the same ratio. So we may put

$$T_1\frac{d}{dT}\frac{\gamma_1(v_1'')^{\frac{2}{3}}}{T_1} = T_2\frac{d}{dT}\frac{\gamma_2(v_2'')^{\frac{2}{3}}}{T_2} = T_3\frac{d}{dT}\frac{\gamma_3(v_3'')^{\frac{2}{3}}}{T_3} = \text{constant},$$

or $$\frac{d}{dT}\gamma_1(v_1'')^{\frac{2}{3}} = \frac{d}{dT}\gamma_2(v_2'')^{\frac{2}{3}} = \frac{d}{dT}\gamma_3(v_3'')^{\frac{2}{3}} = \text{constant}.$$

Hence $$\gamma_1(v_1'')^{\frac{2}{3}} = \gamma_2(v_2'')^{\frac{2}{3}} = \cdots = AT, \qquad 60$$

where A is a constant.

The quantity $\gamma(v'')^{\frac{2}{3}}$ is the molecular surface energy.

Equation 60 enables us to determine the molecular weights of liquids; for if we adjust the surfaces of different liquids until we get the relation of 60, we shall then have the surfaces corresponding to one grammolecule. The constant A is obtained by experiment. The details of the application and corrections must be sought elsewhere.

There is one serious fault in the deduction of 60; namely, in the application of the gas law to saturated vapors. And although the values hereby introduced disappear in the development, the final result is open to criticism.

However, the method has furnished us with some valuable results. According to it the molecules of liquids are generally sim-

ple, sometimes just as simple as the gas molecule, sometimes more complex, but never very complex, hardly more than 4 molecules.

(2) Let v be the molecular volume of a body; that is, the molecular weight divided by the density. The volume occupied by a grammolecule of a substance in dilute solution is given by the following equation,

$$v_0 = \frac{m + W}{d_1} - \frac{W}{d_0}, \qquad 61$$

where v_0 is the desired volume, m the weight of the grammolecule, W the weight of solvent in which the grammolecule is dissolved, d_1 the density of the solution, and d_0 the density of the pure solvent. But the value of v_0 from 61 is such that we must assume that when water is the solvent, the water contracts about 13.5 cc. So that for aqueous solutions,

$$v = v_0 + 13.5. \qquad 62$$

When a molecule of the dissolved body decomposes into two or more molecules, as it often does in water, for every molecule produced, we add 13.5 cc. to v_0 to get v.

By judiciously selecting substances of varying composition, it is possible to find what part of the molecular volume each component occupies in solution.

This can also be done in the solid state, without solution, but on account of the other energies in the solid, the volume relations are much more obscure.

We also find that whenever substances combine in aqueous solution, the molecular volume increases by about 12.4 cc. for every grammolecule produced.

The values for each element or group so far worked out at 15° C., is given in the following table. These values are somewhat variable; it would seem that in an aqueous solution, a benzene ring and a hexamethylene ring have the same minus value, but not in other solvents, as the table shows. They are worked out with assumption that the correction for change in volume of solution is 25.9 cc. for one grammolecule of solute.

Expansion on combination for every grammolecule	12.4 cc.
Correction due to contraction of solvent for every grammolecule	13.5 "
Mol. vol. of bromin	13.2 "
" " carbon	9.9 "
" " chlorin	13.2 "
" " cyanogen	13.2 "
" " hydrogen	3.1 "
" " iodin	13.2 "
" " nitrogen, trivalent	1.5 "
" " " pentavalent	10.7 "
" " " nitro-	9.6 "
" " oxygen, ether, and carbonyl	5.5 "
" " " hydroxyl	2.3 or 0.4 "
" " phosphorus, trivalent	17 "
" " " pentavalent	28.5 "
" " sodium	3.1 "
" " sulfur, as CS or HS	15.5 "
" " " with oxygen	10.7 "
" " hexamethylene ring	− 8.1 "
" " benzene ring	− 13.2 "
" " ethylene bond	− 1.7 "
" " acetylene	3.4 "

When hydroxyl oxygen is united to a carbon atom which is united to another carbon atom in turn united to a hydroxyl, or when hydroxyl oxygen is united to a carbon atom united to carbonyl oxygen, the second value of hydroxyl oxygen is to be used; otherwise, the first.

This table enables us to determine the molecular volume of any substance whose components are in the table. We compute the molecular volume from the table, and then adjust the molecular weight in 63 until it satisfies the equation,

$$v = \frac{m}{s} = \frac{m + W}{d} - \frac{W}{d_0} + 13.5\,x = v_0 + 13.5\,x, \qquad 63$$

where v is the molecular volume calculated from table, s the specific gravity of the body in the state for which the molecular weight is to be determined, and x the number of grammolecules of substance in the solution.

The whole value of these results depends upon the assumption that the contraction on solution is due only to the solvent, and that the molecular volume of the substance is the same in the solid or liquid state as it is in solution. It is very probably so, but it will not do to consider the question settled.

Let n_1, $n_2 \cdots$ be the number of atoms of the different elements in a compound, n the number of carbon rings, v_1, $v_2 \cdots$ the corresponding molecular volumes as given in the table; then

$$v = n_1 v_1 + n_2 v_2 + \cdots + na + 25.9 + 13.5\,(x - 1), \qquad 64$$

where x is the number of grammolecules in the solution, and a is the minus volume for each ring or linking, according to the table.

Problems.

1. What is the molecular volume of $(NH_2)_2CS$ at 15°?

Ans. 66.7 cc.

2. What is the molecular volume of HCOOH at 15°?

Ans. 47.9 cc.

3. What is the molecular volume of $C_6H_4(OH)_2$ at 15°?

Ans. 95.3 cc.

4. An aqueous solution of sodium *m*-amidobenzoate of 3.03 % has a specific gravity of 1.0127 at 15°; what is its molecular weight?

Use equations 63 and 64. The salt decomposes in a water solution into two molecules. *Ans.* 159.

5. The specific gravity of *n*-pentadecane ($C_{15}H_{32}$) is 0.7724; what is its molecular weight? *Ans.* 212.

6. The specific gravity of a hydrocarbon is 0.798, its molecular volume is 298 cc.; what is its molecular weight?

Ans. 238.

7. A hydrocarbon contains carbon and hydrogen in the proportion of 6 to 1. Its molecular volume is 114.4 cc., its specific gravity is 0.729; what is the body?

Ans. Hexamethylen hydrid.

In the case of solvents other than water it would seem that no contraction of solvent occurs, so that 63 becomes

$$v = \frac{m}{s} = \frac{m + W}{d} - \frac{W}{d_0}. \qquad 65$$

In 64 the last term is dropped, as it applies to the decomposition by water, and we get

$$v = n_1 v_1 + n_2 v_2 + \cdots + na + 25.9. \qquad 66$$

The correction 25.9 is retained, for the volumes of constituents are calculated on the basis of this correction.

Problems.

1. The specific gravity of a 13 % solution of a hydrocarbon in acetic acid is 1.020. Specific gravity of acetic acid, 1.051. Proportion of carbon to hydrogen, 12 to 1. Molecular weight, 78. What is it? *Ans.* Benzene.

2. The specific gravity of an 18.8 % solution of a hydrocarbon in benzene is 0.903. Specific gravity of benzene, 0.880. Proportion of carbon to hydrogen, 15 to 1. Molecular weight, 128. What is it? *Ans.* Naphthalene.

We can see from the above examples that this is a valuable method for getting at the constitution of bodies in solution through their specific gravities, but the student is warned against relying too much on this method. There is still a good deal to be done, particularly with other solvents, before we can look upon the volumes in the table on page 58 as being reliable. They are too empirical as yet.

3. There is another way of getting at the molecular weight, which we shall merely state. The theoretical relations are too physical to justify attention in this book.

It has been found that the *critical coefficient*, namely, critical temperature divided by critical pressure (θ_0/π_0), is connected with the molecular weight, thus:

$$\frac{\theta_0}{\pi_0} = \mathrm{AM}\varsigma, \qquad 67$$

where A should be a constant, the same for all bodies; M the molecular weight; ς the refractive index for light waves of infinite length. A varies between 1.6 and 2.2. The critical pressure is to be measured in atmospheres.

52. **Available volumes of liquids.** — The available volume is the volume *unoccupied* by matter or by a collection of energies. Equation 64 can be put in the form

$$v - \Sigma nv = 25.9 = \text{constant} = r, \qquad 68$$

supposing $x = 1$. Comparing with 15, we see that b in that equation corresponds to Σnv in this.

The available volume of a grammolecule of a perfect gas in the gaseous state is the same for all gases under the same conditions. We see by 68 that this is also true for the liquid state, a confirmation of Van der Waals' theory. In this case b and Σnv seem to be identical, for equation 15 is, in form, likewise applicable to the liquid state.

The constant r of 68 has the numerical value 25.9 at 15°. Experiment has shown that at any temperature it has the value

$$r = r_0(1 + 0.00366\, t) = r_0 \frac{T}{273} = 25.9 \frac{273}{288} \cdot \frac{T}{273} = 0.090\, T, \qquad 69$$

where r_0 is its value at 0° C., t temperature centigrade, and T absolute temperature. Hence, *the available volume of a liquid is proportional to its absolute temperature.*

The same law seems to be true for solids, but the available volume of a grammolecule of a solid is either one half that of a liquid, or else a body in the solid state has double the molecular weight that it has in the liquid state.

The available volume of a grammolecule of a gas or vapor is ordinarily greater than that of a grammolecule of a liquid.

Consider a closed vessel containing a grammolecule of a substance partly in the liquid state, partly in the gaseous state. As the temperature increases, the available volume of the liquid increases, while that of the vapor diminishes on account of the increased pressure. At a certain temperature the available volume of each is the same. This temperature coincides with the critical temperature.

The available volume seems to depend somewhat upon the state of the substance. In solution at 15°, its value for different substances varies only slightly from 25.9. In the pure liquid state, not in solution, the variation is more marked, so that this subject needs much more investigation before we can really depend upon numerical values.

53. **The state of a substance in solution.** — The well-known experiment of separating silicic acid from sodium chlorid in a solution shows that a so-called porous substance is not porous to everything. There are a good many substances that are porous, or better, permeable, to some bodies but not to others. We shall call such substances semipermeable, and when in the form of diaphragms, semipermeable diaphragms. By choosing a diaphragm which is permeable to the solvent but impermeable to the solute, we are able to separate them and then mix them again under known conditions in a reversible isothermal cycle, and so determine the available energy belonging to a body in solution.

Let us confine the systems to dilute solutions and thereby avoid the complications due to energies other than volume energy. We made the same restriction for gases.

Let us consider a tube, containing a dilute solution of some

substance, open at the top and provided with a piston, but closed at the bottom by a fixed diaphragm, *a*, permeable to the solvent but impermeable to the solute. The bottom of the tube with diaphragm is in the pure solvent (Fig. 6). The solvent passes through the diaphragm according to the laws of diffusion, as this is permeable to it and the concentration of

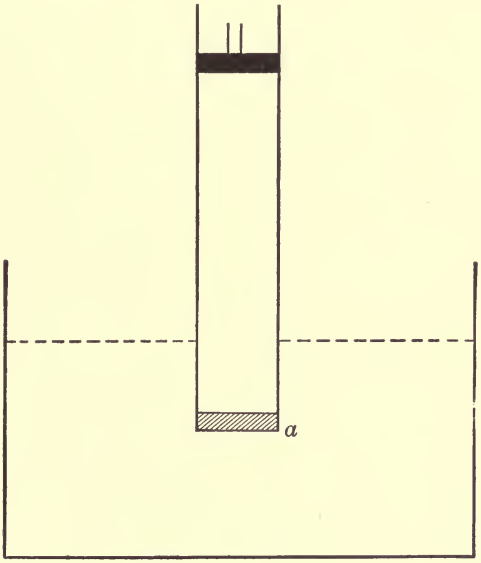

Fig. 6.

the solvent in the solution is less than in the pure solvent. This continues until the weight of the column of liquid prevents any more solvent from entering. The entrance of solvent is, of course, due to the diffusion force which acts in the direction of diminishing concentration of the solvent, and this in turn is due to a substance being in solution. The greater the quantity of this, the greater is the difference in concentration, and the greater the force with which the

solvent enters the tube; consequently, the greater the height of liquid in the tube at equilibrium. If we prevent the solvent from entering at all by a counter pressure, the greater the counter pressure needed.

Experiment shows that for a given substance the counter pressure needed is proportional to the quantity of substance dissolved.

The student should clearly see that the primary cause of the entrance of the solvent is the difference in concentration inside and outside the tube. It is obvious that the concentration is volume concentration.

The pressure on the sides of the tube is due to the solution; but at the bottom, on the semipermeable diaphragm, the pressure is due solely to the substance dissolved, not to the solvent, for this can pass through the diaphragm.

No direct experiment has ever shown the existence of this pressure on the semipermeable diaphragm, but nevertheless we cannot doubt its existence. In no other way can we explain osmotic action nor a large number of other phenomena, nor account for the relations of some forms of energy.

We shall call this pressure on the diaphragm *osmotic pressure.*

The student perceives how very much like a gas we believe a solute to be. Its osmotic pressure varying with the concentration, proportionally, and the concentration varying inversely as the volume of solution, if ϕ is that volume, we may put at constant temperature

$$\pi\phi = \text{constant.} \qquad 70$$

In other words, we see that volume energy, considered the characteristic of the gaseous state, is really a characteristic of a solution, and indeed of the liquid state in general, as we shall see later, and indeed have seen, in the preceding section.

54. **Osmotic pressure and temperature.** — Let us run through a cycle like that used in getting the second law of thermo-

dynamics, using, however, a dissolved substance and a semipermeable diaphragm. The semipermeable diaphragm is supposed to form the bottom of the cylinder. The cylinder is provided with a frictionless piston, whereby we can get work from the system or give it to the system.

We shall limit the changes to infinitesimal changes, thereby simplifying the equation.

(1) Increase isothermally and infinitesimally the volume of the solution, letting an infinitesimal quantity of solvent enter through the semipermeable diaphragm. The piston is pressed back through volume $d\phi$, and as the operation is isothermal, the heat absorbed at temperature T is equal to the work done; so that if π is the osmotic pressure, we have

$$dQ_1 = -\pi d\phi. \qquad a$$

(2) The volume of the solution increases again, but isentropically, so that the temperature decreases to $T - dT$. The heat and work of this operation are

$$dQ_2 = -dW_2. \qquad b$$

(3) The volume of the solution is now decreased isothermally by such an amount that the succeeding isentropic expansion raises the temperature to T. This decrease is $d\phi$, and is done by pressing on the piston, letting the excess of solvent escape through the semipermeable diaphragm. The heat and work of the operation are

$$-dQ_3 = (\pi + d\pi)\, d\phi. \qquad c$$

(4) The solution is compressed again, isentropically, so as to restore initial temperature and volume, thereby completing the cycle. The heat and work of the operation are

$$-dQ_2 = dW_2. \qquad d$$

The available work of the cycle is the sum of a and c; that is,

$$dQ_1 - dQ_3 = dW = d\pi d\phi.$$

The heat put into the system, and which corresponds to Q of equation 42, is $\pi d\phi$. Substituting in 42, we get

$$d\pi d\phi = \pi d\phi \frac{dT}{T},$$

or
$$\frac{d\pi}{\pi} = \frac{dT}{T}, \qquad 71$$

or on integration
$$\pi = aT, \qquad 72$$

where a is a constant.

That is, the *osmotic pressure is proportional to the absolute temperature.* It is evident that the concentration of the solution is supposed to be constant.

This theoretical conclusion has had fair experimental proof.

55. **Avogadro's law.** — Let us conduct a reversible isothermal cycle with the apparatus of Fig. 7.

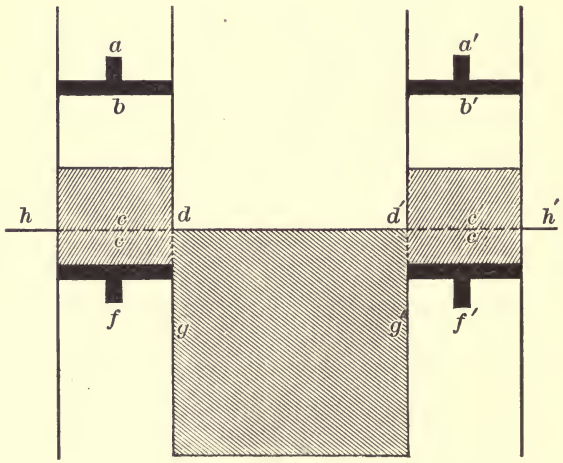

Fig. 7.

Two cylinders, each with two pistons a, f, a', f'. Below a and a' is a free gas b and b'; the gas is the same in each

cylinder, but its pressure in the right cylinder is $p + dp$, while in the other cylinder it is p. Below the gas and in contact with it is its solution in some solvent c, c, c', c'. The solvent is the same in each cylinder. The pressure is greater in one than in the other, and as the gas follows Henry's law,

$$\frac{v_1}{\phi_1} = \frac{v_2}{\phi_2} \text{ or } \frac{p_1}{\phi_2} = \frac{p_2}{\phi_1}, \qquad 73$$

where v_1 and v_2 are the volumes of a grammolecule of gas at pressures p_1, p_2, and ϕ_1, ϕ_2, are the volumes of solutions containing each a grammolecule of gas when the gas pressures are p_1, p_2. The osmotic pressures corresponding to ϕ_1, ϕ_2 are π_1, π_2. Under the solutions are the two diaphragms hd, $h'd'$, permeable to gas but impermeable to solvent. In a side of each cylinder are inserted the two diaphragms dg, $d'g'$, which are permeable to solvent but impermeable to gas. Outside the diaphragm dg, $d'g'$ is the pure solvent.

(1) Raise the piston a and liberate one grammolecule of gas, at the same time raising piston f and thereby driving out so much of the solvent as to keep the concentration of the solution constant. If v is the change of volume due to liberation of m mass of gas, and ϕ the volume of solvent driven out of the solution in this operation, the available work is

$$-p_1v_1 + \pi_1\phi_1.$$

(2) The gas is now allowed to expand to volume v_2. The available work is

$$-\int_{v_1}^{v_2} pdv.$$

(3) It is now put into the right-hand cylinder and driven into solution by compressing with piston a', at the same time lowering piston f' so that solvent can pass in to keep the concentration unchanged. The available work of this operation is

$$+p_2v_2 - \pi_2\phi_2.$$

(4) The dissolved gas at ϕ_2 is now compressed to ϕ_1 in another cylinder with semipermeable diaphragm. The available work of this operation is

$$+\int_{\phi_1}^{\phi_2} \pi d\phi.$$

(5) It is then returned to left-hand cylinder, thus completing the cycle.

Hence, as the cycle is isothermal and reversible,

$$-p_1v_1 + \pi_1\phi_1 - \int_{v_1}^{v_2} pdv + p_2v_2 - \pi_2\phi_2 + \int_{\phi_1}^{\phi_2} \pi d\phi = 0,$$

or

$$\int_{v}^{v_2} pdv = \int_{\phi_1}^{\phi} \pi d\phi. \qquad 74$$

From Henry's law, $dv = d\phi$ in 74, and so when the volume occupied by the grammolecule of substance in the gaseous state and in solution is the same, we have

$$p = \pi. \qquad 75$$

Hence with 70, 73, and 10,

$$\pi\phi = pv = RT, \qquad 76$$

and, *Avogadro's law is also true for substances in solution.*

Problems.

1. 100 grams of sugar are dissolved in 1 liter of solution at 25°. What is its osmotic pressure? *Ans.* 539 cm. Hg.

2. The sp. gr. of a 15 % solution of ethyl alcohol is 0.9777. What is the osmotic pressure of the alcohol in solution at 25°? *Ans.* 5877 cm. Hg.

We see from the last problem that the osmotic pressure, even in a comparatively dilute solution, may be very high. It would break a glass vessel did it reach the walls. But it does not, for experiment shows us that this osmotic pressure is

only exerted *inside* a liquid, and consequently does not act on the walls of the containing vessel which are *outside* the liquid. So soon, however, as we introduce a diaphragm through which the solvent can pass but not the solute, then the osmotic pressure is exerted against it, and is in general very high. This is the chief reason why so few direct measurements of osmotic pressure have been successful.

An explanation of osmotic pressure has been based on the assumption that it is due to tension between the solvent and surface of the pores of the diaphragm, but this idea has not led to any satisfactory conclusion.

56. **Various expressions for the osmotic pressure.** — (1) As the osmotic pressure is due to the solute, it is possible to express it in terms of other properties likewise due to the solute.

We shall proceed to show how π can be expressed in terms of vapor tension for dilute solutions when the solute is not volatile. In concentrated solutions corrections have to be applied.

The inner vessel of Fig. 8 contains a solution of some non-volatile substance. It rises when at equilibrium to a height, h, such that the hydrostatic pressure just balances the osmotic pressure. The tube is closed by a semipermeable diaphragm at the bottom, but is open at the top. It dips into the pure solvent. Over the whole is a bell jar. The air is pumped out, leaving only vapor of the solvent. The vapor pressure of the solution at its surface near the top of the inner vessel is

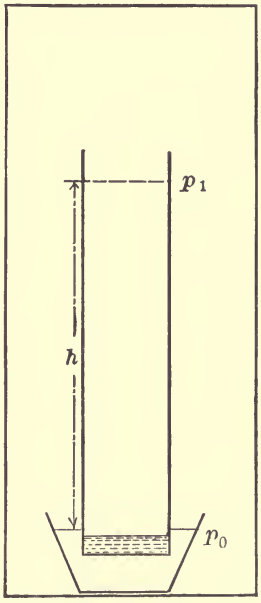

Fig. 8.

p_1, the vapor pressure of the pure solvent at its surface near the bottom is p_0. The temperature is T and kept constant. We have

$$\pi = hs'', \qquad a$$

where s'' is the specific gravity of the solution.

The vapor pressure of the pure solvent at its surface p_0 is just as much greater than its vapor pressure at the height h, as the weight w of the column of vapor of height h and cross section of 1 cm.^{2}; that is, $p_0 = p_1 + w$. Also the vapor pressure of the solvent at the height h above its surface just equals the vapor pressure of the solution at its surface near the top of the inner tube. Hence the vapor pressure of pure solvent at the level of the solution is p_1, and so

$$\int_{p_0}^{p_1} dp = \int_0^h s' dh,$$

where s' is the specific gravity of the vapor, and p_1 is the vapor pressure of solution or of solvent at height h above the surface of the solvent. But

$$s' = \frac{M}{v} = \frac{Mp}{RT},$$

where M is the molecular weight of the vapor and v the volume of a grammolecule of vapor; so

$$-\int_{p_0}^{p_1} \frac{dp}{p} = \frac{M}{RT} \int_0^h dh,$$

or

$$h = -\frac{RT}{M} l \frac{p_1}{p_0} = \frac{RT}{M} l \frac{p_0}{p_1}.$$

Substituting in a,

$$\pi = \frac{RT}{M} s'' l \frac{p_0}{p_1}, \qquad 77$$

which expresses π in terms of vapor pressure of solvent and solution.

The quantities R, T, M, s'', are all positive; hence, as π is positive, *the vapor pressure of a solution is less than the vapor pressure of the pure solvent.*

As the solution is dilute, s'' is sensibly the same as the specific gravity, s, of the solvent, and so, at constant temperature, for the same substance,

$$\frac{RT}{M}s = \text{constant.}$$

Now the osmotic pressure is proportional to the number of grammolecules of solute in a fixed volume of solution, let us say 1000 cc. Hence, we may put, if A is a constant and n the number of grammolecules dissolved in 1000 cc.,

$$n = Al\frac{p_0}{p_1} = A\frac{p_0 - p_1}{p_1} = N\frac{p_0 - p_1}{p_1},$$

where N is the number of grammolecules of solvent in which n grammolecules of substance are dissolved, for experiment has shown that numerically $A = N$.

Transforming, $$\frac{n}{N+n} = \frac{p_0 - p_1}{p_0}. \qquad 78$$

We can calculate from 77 the relative depression in vapor pressure in a solution containing one grammolecule of substance in 1000 cc. at 0° C. In this case π becomes $22.222 \cdot 76$ cm. Hg.

$$22.222 \cdot 76 = \frac{22222 \cdot 76}{273} \cdot \frac{273}{M} s''l\frac{p_0}{p_1},$$

or $$\frac{p_0 - p_1}{p_1} = \frac{1}{1000} \cdot \frac{M}{s''}. \qquad 79$$

(2) From 52 we have

$$\frac{dp}{p} = \frac{Q}{R}\frac{dT}{T^2}. \qquad 80$$

As a solution has a lower vapor pressure than the pure solvent, to bring the vapor pressure of a solution up to the vapor pres-

sure of the pure solvent, the temperature of the solution must be raised. So that the effect of dissolving a non-volatile substance is to change dp and dT in opposite ways; hence

$$\frac{dp}{p} = -\frac{Q'}{R}\frac{dT}{T^2},$$

where Q' is the heat of vaporization. Integrating between p_0 and p_1, T_0 and T_1, we have

$$\int_{p_1}^{p_0}\frac{dp}{p} = -\frac{Q'}{R}\int_{T_1}^{T_0}\frac{dT}{T^2},$$

or

$$l\frac{p_0}{p_1} = \frac{Q'}{R}\frac{T_1 - T_0}{T_0 T_1}. \qquad 81$$

The student should thoroughly understand the relations of p and T. The quantities p_0 and T_0 refer to the pure solvent; p_1 is the vapor pressure of the solution, and on account of the depression of the vapor pressure, if we are to get the vapor pressure of the solution up to p_0, we must heat it to T_1, so that T is not the temperature at which the solution has the vapor pressure p_1, but the temperature to which it must be heated to raise its vapor pressure to p_0. It is convenient to make p_0 the atmospheric pressure, in which case T_0 and T_1 become the boiling temperature of pure solvent and solution respectively.

Substituting in 77,

$$\pi = \frac{Q'}{M}s''\frac{T_1 - T_0}{T_1}, \qquad 82$$

for $T = T_0$.

To calculate the change in boiling temperature produced by dissolving one grammolecule of a non-volatile solid in a liter of solution at T_1, we have, as before,

$$\frac{22.222 \cdot 76 \cdot 13.6\, T_1}{42750 \cdot 273} = \frac{Q's''(T - T_0)}{MT_1},$$

or putting $T_1 - T_0 = t'$, we have

$$t' = \frac{22.222 \cdot 76 \cdot 13.6}{42750 \cdot 273}T_1^2\frac{M}{Q'}\frac{1}{s''} = 0.001967\, T_1^2\frac{M}{Q's''}. \qquad 83$$

When a solution and the frozen solvent coexist, the vapor pressure of the frozen solvent must equal the vapor pressure of the solution. Let p_0'' be the vapor pressure of the pure solvent at its freezing point T_0, and p_1'' its vapor pressure at T_1. This, T_1, is the temperature at which the *solution* freezes. The solvent is supposed to be undercooled. An *undercooled* liquid is a liquid cooled *below* its freezing point without letting it freeze. Integrating 80 between these limits, we have

$$\int_{p_1''}^{p_0''} \frac{dp}{p} = \frac{Q_1}{R} \int_{T_1}^{T_0} \frac{dT}{T^2}, \qquad a$$

where Q_1 is the heat of vaporization of solvent; T_1, the temperature to which the solution is raised to bring its vapor pressure up to that of the solvent at the freezing point T_0 of the solvent.

Similarly for the frozen solvent, we have

$$\int_{p_1'''}^{p_0'''} \frac{dp}{p} = \frac{Q_2}{R} \int_{T_1}^{T_0} \frac{dT}{T^2}, \qquad b$$

where p_0''' is the vapor pressure of the frozen solvent at T_0; p_1''', its vapor pressure at T_1; Q_2, the heat of sublimation of the frozen solvent.

Subtracting b from a, we have

$$\int_{p_1''}^{p_0''} \frac{dp}{p} - \int_{p_1'''}^{p_0'''} \frac{dp}{p} = \frac{Q_1 - Q_2}{R} \int_{T_1}^{T_0} \frac{dT}{T^2};$$

or, since $p_0'' = p_0'''$, for the frozen solvent and liquid solvent can coexist at T_0, we have

$$\int_{p_1''}^{p_1'''} \frac{dp}{p} = \frac{Q_1 - Q_2}{R} \int_{T_1}^{T_0} \frac{dT}{T^2}.$$

Now, since frozen solvent and solution can coexist at T_1, p''' becomes equal to the vapor pressure of solution at T_1, which we have called p_1. p_1'' is the vapor pressure of pure solvent at the

same temperature, which we have called p. $Q_2 - Q_1$ is the heat of fusion of solvent; call it Q''. Then

$$l\frac{p_0}{p_1} = \frac{Q''}{R}\left(\frac{1}{T_1} - \frac{1}{T_0}\right).$$

Substituting in 77, we have

$$\pi = \frac{Q''}{M} s'' \frac{T_0 - T_1}{T_1}. \qquad 84$$

As before we get for t'', the depression in the freezing point of the solvent produced by one grammolecule of substance in 1000 cc. of solvent,

$$t'' = 0.001967\ T_1^2 \frac{M}{Q''s''}. \qquad 85$$

57. **Molecular weights of dissolved bodies.** — Any equation from 76 to 78 and 82 to 85 gives the molecular weight of any solute, which must be non-volatile when vapor tension is involved. In the freezing methods, the solute may be volatile or not, it makes no difference. The equation to be chosen depends upon the data at hand. In general, 83 and 85 are used in a somewhat modified form. In regard to 83, instead of dissolving the grammolecule in a 1000 cc. of solution, it is dissolved in 100 grams of solvent. When the solution is dilute, as it should in general be, the specific gravity of solutions and solvent are so nearly the same that we put volume of solution $= 100/s''$, and T_1 is so near T_0 that we put $T_1 = T_0$. The heat of vaporization is made to refer to a gram, and so $Q' = q'M$, where q' denotes the heat of vaporization of one gram of solvent. So the rise in boiling temperature for one grammolecule of solute in 100 grams of solvent is

$$t' = \frac{0.001967 \cdot T_0^2\, 1000 \cdot s''}{q's'' \cdot 100} = \frac{0.02\ T_0^2}{q'}, \qquad 86$$

where T_0 is the boiling temperature of pure solvent.

Similarly for 85,

$$t'' = \frac{0.02\, T_0^2}{q''}, \qquad 87$$

where T_0 is the freezing temperature of pure solvent, and q'' the heat of fusion.

These are the changes in T made by one grammolecule of solute in 100 grams of solvent; so if we denote the molecular weight of the solute by m, and t_1', t_1'', are the changes in boiling temperature and freezing temperature made by w of the substance in 100 grams of solvent,

$$m = \frac{t'}{t_1'} w, \text{ or } m = \frac{t''}{t_1''} w. \qquad 88$$

The heats q' and q'' have not been determined for every solvent by experiment, but we can compute them from 48, 50, or 52, when dp/dT is known. When this is not possible, when dp/dT is not known, we dissolve a grammolecule of some body whose molecular weight has been determined in a good many solvents, and consequently whose behavior is understood, and in that empirical way find t' and t''.

The details and corrections for determinations of molecular weights in these ways must be sought elsewhere.

Problems.

1. For cymene, $q' = 69.82$ cals., $T_0 = 446$. What is t'?
Ans. 56.96°.

2. For carbon disulfid, $T_0 = 323$ when $p = 731$ mm. Hg, $dp/dT = 23.73$ mm. Hg. What is t'? *Ans.* 23.41°.

3. For naphthalene, $q'' = 35.6$ cals., $T_0 = 352$. What is t''?
Ans. 69.6°.

4. For acetic acid, $T_0 = 290$ when $p = 760$ mm. Hg, $dp/dT = 314050$ mm. Hg, $v'' - v''' = 9.57$ cc. What is t''?
Ans. 36.41°.

5. 2.411 grams of a substance are dissolved in 22.22 grams of benzene; $t_1'' = 4.345°$, $q'' = 29.09$, $T_0 = 275$. What is its molecular weight? *Ans.* 129.8.

6. When aluminium hydroxid is added to an aqueous solution of KOH or NaOH, it dissolves. The reaction may be either

$$KOH + Al(OH)_3 = Al(OH)_2OK + H_2O,$$

or $$2\,KOH + AL_2(OH)_6 = Al_2(OH)_4(OK)_2 + 2\,H_2O.$$

The freezing point of KOH or NaOH solution is not changed by addition of aluminium hydroxid. Which of these reactions takes place? Why?

58. **Liquid and vapor.** — Let n denote the number of gram-molecules of a substance dissolved in N grammolecules of solvent. Then according to 78,

$$\frac{n}{N} = \frac{p_0 - p_1}{p_1}, \text{ or } \frac{n}{N+n} = \frac{p_0 - p_1}{p_0}. \qquad 89$$

Now we may look upon the vapor of a solvent as existing in the solvent in the same state that any other substance would be in when dissolved in that solvent. Its concentration is, therefore, measured by its osmotic pressure. Let π_0, ϕ_0, denote respectively osmotic pressure and osmotic volume of the dissolved vapor in the pure solvent; π_1, ϕ_1, the same quantities when a substance besides the vapor is in solution; p_0, v_0, the pressure and volume of the vapor in contact with the pure solvent; p_1, v_1, the same quantities when a substance besides the vapor is in solution.

(1) By means of a semipermeable diaphragm let a gram-molecule of dissolved vapor pass from the pure solvent. The available work is

$$-\pi_0\phi_0 = -RT.$$

(2) Let the grammolecule of dissolved vapor expand till it has a pressure π_1. The available work is

$$-\int_{\pi_1}^{\pi_0}\phi d\pi = -RTl\frac{\pi_0}{\pi_1}.$$

(3) Let it then pass into the solution. The available work is

$$+\pi_1\phi_1 = +RT.$$

(4) Let x grammolecules pass out of the solution in the form of vapor. The available work is

$$-xp_1v_1 = -xRT,$$

where x is the number of grammolecules of gaseous vapor necessary to make one grammolecule of dissolved vapor.

(5) Let the x grammolecules of vapor be compressed until the pressure equals p_0. The available work is

$$+x\int_{p_1}^{p_0}vdp = +xRTl\frac{p_0}{p_1}.$$

(6) Let the x grammolecules be driven into the pure solvent. The available work is

$$+xp_0v_0 = xRT.$$

The cycle is now complete, and so

$$\frac{\pi_0}{\pi_1} = \left(\frac{p_0}{p_1}\right)^x. \qquad 90$$

Let us assume that $x = 1$. From the investigations according to the methods of § 51, it would appear that $x > 1$. If further investigation confirms this it will be easy to change x.

We commonly assume that there is empty space between the particles of liquid; this is the space we shall consider occupied by the dissolved vapor when only the pure solvent is present. When an additional body is dissolved in the solvent, a portion of this space is occupied by the dissolved body, and the dissolved vapor is forced to give way, and consequently

its concentration diminished in proportion to the number of molecules of the other substance in solution; that is, if ν is the number of molecules of dissolved vapor at any time, and n the number of molecules of some other substance in solution at the same time,

$$\nu + n = \text{constant.}$$

If c_0 is the concentration of the dissolved vapor when alone in the liquid, and c_1 its concentration after the new substance has been added, then $c_0 - c_1$ will be the decrease in concentration of the dissolved vapor due to the addition of the n gram-molecules of substance. We have, therefore,

$$\frac{c_0 - c_1}{c_0} = \alpha \frac{n}{\nu + n};$$

also

$$\frac{c_0}{c_1} = \frac{\pi_0}{\pi_1},$$

and when $x = 1$,

$$\frac{\pi_0}{\pi_1} = \frac{p_0}{p_1}.$$

From these we have

$$\frac{p_0 - p_1}{p_0} = \alpha \frac{n}{\nu + n}.$$

With 89,

$$\alpha \frac{n}{\nu + n} = \frac{n}{N + n}. \qquad 91$$

As this equation is true for any small value of n, it is true when n is so small that it vanishes in comparison with ν and N. We then get

$$\frac{\alpha n}{\nu} = \frac{n}{N} \text{ or } \alpha = \frac{\nu}{N}.$$

Substituting in 90,

$$\nu = N. \qquad 92$$

That is, when $x = 1$, the molecular concentration of the dissolved vapor is the same as the molecular concentration of the liquid; in other words, all the solvent is to be considered as dissolved vapor. This means that the liquid is not simply

to be looked upon as a condensed gas in the sense that it is matter compressed into smaller space, but condensed in the sense that the gaseous activity, pressure, is carried into the liquid condition; and we are to treat a liquid as we would a gas. That is, there is the same volume energy in a liquid that there is in a gas, only we have to use other means to recognize it; namely, osmotic means. Therefore when a substance dissolves it passes into a medium which is in a gaseous state, so far as osmotic energy is concerned, and the dissolved substance itself naturally shows a gaseous nature.

Assuming that $x = 1$, we can calculate the osmotic pressure of the liquid.

Problems.

1. What is the osmotic pressure of water at 25°? Sp. gr. of water = 0.9971 at 25°. *Ans.* 1021 m. Hg.

2. What is the osmotic pressure of methyl alcohol at the same temperature? Sp. gr. = 0.79 at 25°. *Ans.* 455 m. Hg.

59. **Molecular weights of bodies which give off vapor when in solution.** — In deriving 78 we assume that the solute does not produce vapor of its own. We shall now proceed to consider a case in which the solute does give off vapor of its own. The theoretical expression is very simple; for in deriving the preceding equations the solvent has been the component of the solution which separated as vapor on heating, or as solid on freezing. Consequently, when there are two bodies in solution, both of which produce vapor, we are to consider each in turn as solvent and solute. The total calculated depression subtracted from the sum of the vapor pressures of the two components taken separately leaves the vapor pressure of the solution.

Example. — 15.18 grammolecules of chlorbenzene are dissolved in 84.82 grammolecules of benzene. What is the vapor

pressure of the mixture at 34.8°? Vapor pressure of chlorbenzene at 34.8° is 20.3 mm. Hg; vapor pressure of benzene at same temperature is 145.4 mm. Hg.

Let n_1 be the number of grammolecules of chlorbenzene, and n_2 the number of grammolecules of benzene in the solution, so that $n_1 + n_2 = 100$. Hence, depression Δp_1 of benzene by chlorbenzene is

$$\frac{n_1}{n_1 + n_2} = \frac{\Delta p_1}{p_0} \text{ or } \Delta p_1 = \frac{15.18}{100} 145.4 = 22.1 \text{ mm. Hg};$$

similarly, depression Δp_2 of vapor of chlorbenzene by benzene is

$$\Delta p_2 = \frac{84.82}{100} 20.3 = 17.2 \text{ mm. Hg.}$$

Total depression = 39.3 mm. Hg. Vapor pressure of solution, if neither constituent affected vapor pressure of the other, = 145.4 + 20.3 = 165.7 mm. Hg. Hence vapor pressure of mixture = 165.7 − 39.3 = 126.4 mm. Hg.

Problems.

1. 41.82 grammolecules of chlorbenzene in 100 grammolecules of a solution in toluene. What is the vapor pressure of the solution at 34.8°? Vapor pressure of toluene is 46.8 mm. Hg at that temperature. *Ans.* 35.7 mm. Hg.

2. Vapor pressure of a solution is 105.7 mm. Hg at 34.8°. Vapor pressures of the pure constituents are 145.4 mm. Hg and 8.0 mm. Hg respectively, at 34.8°. How many grammolecules of one are mixed with how many grammolecules of the other to make 100 grammolecules of solution?

Ans. 28.9 grammolecules and 71.1 grammolecules.

In these problems we assume that the molecular weight of each body in the solution is the same as the molecular weight which enters into chemical reaction. But of course in most cases we do not know this, and the problems are usually in the

form of known vapor pressure and unknown molecular weight. In such cases we learn as much as we can about each constituent separately, in as many ways as possible; by determining its critical values and comparing with the theoretical values of Von der Waals' theory, how far its vapor density deviates from the law of gases, what its molecular weight is in solutions so dilute that the vapor pressure of the solute is an insignificant fraction of the whole vapor pressure, etc.

Example. — 30.33 grammolecules of brombenzene are contained in 100 grammolecules of a solution in benzene. The calculated vapor pressure of the solution is 103.7 mm. Hg, the observed vapor pressure is 105.7. Some very careful and thorough experiments have been made with both these bodies separately. Brombenzene behaves as it should, benzene does not. We therefore assume that the molecule of brombenzene is normal in this case also, and that the difference between calculated and observed pressure is due to the benzene. Vapor pressure of brombenzene = 8.0 mm. Hg; vapor pressure of benzene = 145.4 mm. Hg. Both pure and at 34.8°.

The depression due to brombenzene is

$$\Delta p_1 = \frac{30.33}{100}\ 145.4 = 44.1 \text{ mm. Hg.}$$

Hence depression due to benzene Δp_2 is $(153.4 - 105.7) - 44.1 = 3.6$ mm. Hg. If m_1' is the molecular weight of brombenzene and m_2' that of benzene in the solution, while m_1, m_2 are respectively the ordinary molecular weights, n_1, n_2, the number of grammolecules of each in the solution, we have

$$n_1 = \frac{30.33\, m_1}{m_1'} = 30.33, \text{ since } m_1' = m_1,$$

$$n_2 = \frac{69.67\, m_2}{m_2'} = \frac{69.67 \cdot 78}{m_2'}, \text{ since } m_2 = 78 \text{ and } m_2' \text{ not } = m_2.$$

So we may write 78

$$\frac{\frac{69.67 \cdot 78}{m_2'}}{\frac{30.33 + 69.67 \cdot 78}{m_2'}} = \frac{3.6}{8},$$

which gives $m_2' = 219.$

So, in such concentrations, the benzene molecule seems to be polymerized nearly 3 times.

PROBLEM.

In the following problem assume first that one constituent is normal and then that the other constituent is normal.

Grammolecules of $CHCl_3$ in 100 grammolecules of solution in C_6H_6.	Vapor pressure of solution at 34.8° in mm. Hg.
16.97	163.1
50.53	205.0
59.47	221.4

Vapor pressure of pure chloroform = 289.2 mm. Hg, vapor pressure of pure benzene = 145.4 mm. Hg, both at 34.8°. What are the molecular weights of the two bodies?

Ans. When chloroform is normal, benzene = 65.4, 65.1, 68.1;
" benzene " " chloroform = 100.5, 83.3, 90.1.

60. **Heat of solution.** — We exclude all chemical action. Then solution should be identical with sublimation or vaporization. In the first case 49 is to be used; in the second case, 50 or 51.

Let the two bodies which compose the solution be A and B. They are contained in vessels 1 and 2 of Fig. 9. The solution contains n grammolecules of A to one grammolecule of B.

(1) Vaporize isothermally n grammolecules of A and one grammolecule of B. The available work is

$$-np_1v_1 - p_2v_2,$$

where p_1, v_1, p_2, v_2 are respectively pressure and molecular volume of the two vapors.

(2) Expand each vapor isothermally to the pressure it has in contact with the solution. Call these pressures p_1', p_2'. The available work is

$$-nRTl\frac{p_1}{p_1'}-RTl\frac{p_2}{p_2'}.$$

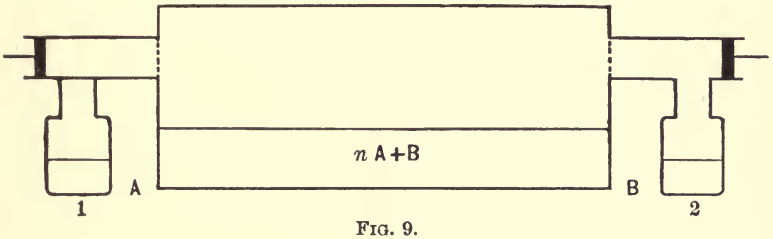

FIG. 9.

(3) With a cylinder and piston and semipermeable diaphragm drive isothermally each vapor into the inner vessel in the proper proportions. This vessel contains some solution and saturated vapor of course. As the new vapor comes in, a corresponding quantity of vapor condenses and mixes with the solution. The available work is

$$+np_1'v_1'+p_2'v_2'.$$

The sum of these quantities gives the total available work of the operation; namely,

$$-RT\left(nl\frac{p_1}{p_1'}+l\frac{p_2}{p_2'}\right)=W. \qquad 93$$

This gives

$$dW=-R\left(nl\frac{p_1}{p_1'}-l\frac{p_2}{p_2'}\right)dT-RTd\left(l\frac{p_1}{p_1'}+l\frac{p_2}{p_2'}\right),$$

which substituted in 42 gives

$$Q=-RT\left(nl\frac{p_1}{p_1'}+l\frac{p_2}{p_2'}\right)-RT^2\frac{d}{dT}\left(nl\frac{p_1}{p_1'}+l\frac{p_2}{p_2'}\right). \qquad 94$$

But this Q is not the heat of solution; it is the heat of the

whole operation of mixing the liquids and includes the available energy coming from the mixing as well as the heat of solution. The latter is the change of internal energy which we have denoted by U. So

$$Q = U + W,$$

and hence, with 93 and 94,

$$U = Q_0 = RT^2 \frac{d}{dT}\left(nl\frac{p_1}{p_1'} + l\frac{p_2}{p_2'}\right), \qquad 95$$

where Q_0 is the heat of solution.

When one constituent has no vapor tension, the equation reduces to

$$Q_0 = RT^2 \frac{d}{dT} l\frac{p_1}{p_1'}. \qquad 96$$

When $Q_0 = 0$,

$$\frac{d}{dT} l\frac{p_1}{p_1'} = 0. \qquad 97$$

That is, when there is no chemical action and the heat of solution of a solute is zero, the ratio of vapor pressures of pure solvent and solution is independent of T. This might be predicted, for as heat is not connected with solution, heat will not affect the condition of the solution.

61. **Heat of dilution and available energy.** — Let us consider from another point of view how much energy is available on diluting a solution of some non-volatile solute, or, more correctly, how much energy is available in the operation of removing one grammolecule of solvent from a solution of one concentration, and adding the grammolecule so removed to another solution containing the same constituents, but in different proportion.

Let Q be the total heat of any operation, or the total energy of any operation; W, the available energy; and U, the change in internal energy. We have, from the first law of thermodynamics,

$$Q = W + U.$$

Substituting in 42, and rearranging,

$$W + U = T\frac{dW}{dT}. \qquad 98$$

In this particular case, U = heat of dilution = Q_0.

When $$T\frac{dW}{dT} = 0, \qquad 99$$

then $$W = -Q_0, \qquad 100$$

and the available energy equals the heat of the operation.

Example. — The available energy in conveying one gram-molecule of H_2O from an aqueous solution of H_2SO_4 at T, of vapor pressure p_1 to one of vapor pressure p_2, at the same temperature, is

$$W = RTl\frac{p_1}{p_2}. \qquad 101$$

The heat developed on mixing a solution containing one gram-molecule H_2SO_4 with n grammolecules H_2O is, in calories,

$$Q_0 = \frac{n\,17860}{n + 1.8}. \qquad 102$$

This is an empirical equation. The vapor pressure of a solution composed of $H_2SO_4 + H_2O$, one grammolecule each, is at $25° = 0.0184$ cm. Hg; that of a solution $H_2SO_4 + 2\,H_2O$ is 0.1125 cm. Hg at the same temperature. Hence,

$$W = RTl\frac{p_2}{p_1} = 1340\,l\frac{0.1125}{0.0184} = 1053 \text{ cals.},$$

where Briggs' logarithms are used.

From 102 we get for the quantity of heat involved in transferring one grammolecule of H_2O from solution of concentration $n = 1$ to that of concentration $n = 2$, in calories,

$$\left(\frac{dQ_0}{dn}\right)_{n=2} - \left(\frac{dQ_0}{dn}\right)_{n=1} = 1874 \text{ cals.}$$

These numbers do not agree well, but this is probably owing to inaccuracy in the measurement of p.

Since, by condition, $dW/dT = 0$, we may use data for p obtained at any reasonable temperature. Some very accurate measurements have been made of the vapor tension of $H_2SO_4 + nH_2O$ in cm. Hg at 100° C. They are,

$n = 6.94$, $p = 41.68$; $n = 11.11$, $p = 56.16$;
$n = 7.94$, $p = 46.40$; $n = 13.89$, $p = 61.20$.
$n = 9.26$, $p = 51.30$;

Problems.

1. Calculate from these data the heats of dilution and available energy. *Ans.* $Q_0 = 82, 76, 70, 64$; $W = 80, 75, 68, 62$.

In this case the agreement is much better, and we may conclude that 99 and 100 are true in this case.

2. Why is the differential coefficient of Q_0 used, and not Q_0?

CHAPTER V.

EQUILIBRIUM.

62. **Equilibrium.** — A system is in equilibrium when in two consecutive units of time the state of the system does not in anywise change. The equilibrium is stable when, after a small forced change, the change does not continue; the equilibrium is unstable when the forced change does continue. When the forced change necessary to produce the continued change is very small, the equilibrium is very unstable, and the larger the forced change necessary to do this, the nearer the equilibrium is to stable equilibrium. Stable equilibrium is marked by a voluntary return of the system to the initial state when the cause of the small forced change is removed.

63. **Conditions of equilibrium.** — The condition of equilibrium for a system is

$$dU \geqq 0, \tag{103}$$

when the change of entropy is zero; that is, when the system neither absorbs nor gives out heat.

When the change of entropy is not zero, then the condition of equilibrium for the system is

$$dS \leqq 0, \tag{104}$$

when the change of internal energy is zero.

When the system is in unstable equilibrium,

$$dU = dS = 0. \tag{105}$$

Equations 103, 104, 105, are expressions of experience; they are altogether empiric.

For our purpose it is better to put these conditions of equilibrium in a somewhat different form.

Consider a system composed of solids in contact either with a solution or with gases, and in equilibrium. Let the chemical equation or the chemical reaction be

$$aA + bB + cC + \cdots + fF + gG + \cdots = a'A' + b'B' + c'C' + \cdots + f'F' + g'G' + \cdots, \quad 106$$

where A, B, C, $\cdots$ are the initial solids, F, G, $\cdots$ either the initial bodies in the solution or the initial gases, A', B', C' $\cdots$ the final solids, F', G' $\cdots$ the final bodies in solution or the final gases, and the small letters are the respective numbers of grammolecules which enter into the reaction.

Starting with the system in equilibrium, introduce a certain quantity of the initial bodies in the proportion indicated by the equation, and to avoid any disturbance through change in concentration, remove the products as fast as formed. This can always be done in imagination, if not in practice. The addition and removal of the *solids* is to be considered as a mechanical operation involving no energy. The whole operation is to be conducted reversibly and isothermally. The liquids and dissolved bodies are added and removed by the semipermeable diaphragm, the gases in the ordinary way.

The available work of driving into the system f grammolecules is $+fRTl\frac{\pi}{\pi_0}$, where π is the pressure in the system, and π_0 the standard pressure outside the system. It is osmotic pressure if a solution, gaseous pressure if a gas. As π_0 is fixed, we see that π/π_0 is proportional to the volume concentration of F in the solution, so we may put the available work in the form $+fRTlc_1$. Similarly for the other bodies in solution, and so the total available work of 106 is

$$W = RT(flc_1 + glc_2 + \cdots - f'lc'_1 - g'lc'_2 - \cdots) = RTl\frac{c_1^f c_2^g \cdots}{c_1'^{f'} c_2'^{g'} \cdots}.$$

When the system is composed of liquids and gases, we proceed in a similar way and get the same final expression, remembering, however, to make the distinction between osmotic quantities and gaseous quantities.

As the operation is reversible and isothermal, W is dependent only on the initial and final states, and consequently

$$W = RTl\frac{c_1^{f}c_2^{g}\cdots}{c_1'^{f'}c_2'^{g'}\cdots} = \text{constant}, \qquad 107$$

or

$$K = \frac{c_1'^{n_1'}c_2'^{n_2'}\cdots}{c_1^{n_1}c_2^{n_2}\cdots}, \qquad 108$$

where K is a constant. The accented quantities are the products, the unaccented quantities the initial bodies. The student should remember that c is the concentration *at equilibrium*, and n_1, n_2, $\cdots$ substituted for f, g, $\cdots$ are the number of grammolecules reacting in the chemical equation 106. We shall call equation 108 the *equilibrium equation*. An equilibrium equation corresponds to a chemical reaction that ceases before *any* of the initial bodies have disappeared.

Equation 108 is formulated thus: *When a system is in equilibrium, the ratio between the concentrations of the initial bodies, each raised to a power equal to the number of molecules of the body reacting in the chemical reaction, and the concentration of the products, each raised to a power equal to the number of molecules of the body reacting in the chemical reaction, is constant.* The student should not forget that 108 is only true for constant T; how K changes with T will appear later.

Equation 108 may also be obtained in this way, which leads to an important connection of K with T. Let v be the velocity with which the initial bodies react to produce the final bodies. By velocity is meant the ratio of grammolecules of product to time in which they are produced. Assuming that v is proportional to the concentration,

$$v = kc_1^{n_1}c_2^{n_2}\cdots. \qquad 109$$

Let v' be the velocity with which the initial bodies are reproduced from the products,

$$v' = k' c_1'^{n_1'} c_2'^{n_2'} \ldots. \qquad 110$$

At equilibrium, $v = v'$, and so

$$K = \frac{k}{k'} = \frac{c_1'^{n_1'} c_2'^{n_2} \ldots}{c_1^{n_1} c_2^{n_2} \ldots}, \qquad 111$$

which is identical with 108.

All chemical reactions are not always equilibrium reactions. This may be on account of the temperature, for many reactions which proceed until one of the initial bodies entirely disappears at the ordinary temperature, become equilibrium reactions at some other temperature. So it is not at all impossible that all reactions are equilibrium reactions or not, according to the temperature. It is also possible that the initial bodies never entirely disappear, but that their quantity is so small in many reactions that their presence cannot be detected.

64. **Equilibrium in gaseous systems.** — These are the simplest systems.

Consider hydriodic acid. The chemical reaction is

$$2\,HI = H_2 + I_2. \qquad 112$$

At equilibrium,

$$2\,HI = 2\,(1 - x)\,HI + xH_2 + xI_2, \qquad 113$$

where x is the fraction of a grammolecule of the initial body which decomposes. We shall call it the *degree of decomposition;* it is often called the *degree of dissociation* when the products occupy a larger volume than the initial bodies. Let c_1 refer to HI, c_1' to H_2, and c_2' to I_2. Then $c_1 = (1 - x)/v$, $c_1' = x/v_1$, $c_2' = x/v$, $n_1 = 2$, $n_1' = 1$, $n_2' = 1$, and 108 becomes

$$K = \frac{x^2}{4\,(1 - x)^2}. \qquad 114$$

When one or more of the products are already present at the outset, say a grammolecules of H_2 and b grammolecules of I_2, 108 becomes

$$K = \frac{(x+a)(x+b)}{4(1-x)^2}. \qquad 115$$

We may express K in pressure instead of in concentration, or in x. In this case $c_1 = p_1$, $c_1' = p_1'$, $c_2' = p_2'$, and 108 becomes

$$K = \frac{p_1' p_2'}{p_1^2}. \qquad 116$$

In this particular system equilibrium is independent of c or of p. For suppose we start with n grammolecules of HI; then 114 and 116 become respectively

$$K = \frac{n^2 x^2}{4n^2(1-x)^2}, \text{ and } K = \frac{np_1' np_2'}{n^2 p_1^2},$$

which are the same as 114 and 116. This conclusion is confirmed by experiment.

At 440°, $x = 0.28$. Substituting in 114 gives $K = 0.0377$.

Example. — Hydrogen at 177 cm. Hg is in contact with I vapor at 138 cm. Hg in a closed vessel. What proportion of H forms HI? Suppose a grammolecule of H has just the pressure 177 cm. Hg. When brought into the I vapor, combination takes place, and continues until the pressures of the three constituents satisfy 116. If y is the fraction of a grammolecule of H which forms HI with the I, we have for p_1, the pressure of the HI, the value

$$p_1 = y\,2 \cdot 177;$$

for p_1', the pressure of the uncombined H,

$$p_1' = (1-y)177;$$

for p_2', the pressure of the uncombined I,

$$p_2' = 138 - y\,177.$$

Substituting in 116 gives with the known value for K,

$$0.0377 = \frac{(1-y)177\,(138-y177)}{(y\,2\cdot 177)^2},$$

wherefore $$y = 0.62.$$

Problems.

1. The initial pressure of H is 176 cm. Hg, the initial pressure of I is 45.3 cm. Hg. What proportion of H combines to form HI? *Ans.* $y = 0.25$.

2. The initial pressure of I is 38.2 cm. Hg, $y = 0.82$. What is the initial pressure of the H? *Ans.* 28 cm. Hg.

It is often convenient to get x from a measurement of the density instead of the pressure. Let the chemical reaction be

$$aA = bB + cC + dD + \cdots,$$

where a, b, c, d, $\cdots$ are the numbers of molecules of A, B, C, D, $\cdots$. Let the condition of equilibrium be

$$aA = a(1-x)A + xbB + xcC + xdD + \cdots.$$

Then if Δ be the actual observed density, and ∂ the calculated density according to Avogadro's law, assuming no decomposition to have occurred,

$$\Delta = \frac{W}{a(1-x)v + xbv + xcv + xdv}, \text{ and } \partial = \frac{W}{av},$$

where v is the volume of a grammolecule and W the mass of the initial body, which is also the mass of the products taken as a whole. Hence

$$x = \frac{(\partial - \Delta)a}{\Delta(b + c + d + \cdots - a)}. \qquad 117$$

This equation fails when $b + c + d + \cdots = a$.

Problems.

1. The observed density of N_2O_4 is 1.663 compared to air. The chemical reaction is

$$N_2O_4 = 2\,NO_2.$$

What is x? *Ans.* 0.92.

2. What is observed density of N_2O_4 compared to air when $x = 0.630$? *Ans.* 1.96.

3. Apply 117 to decomposition of HI and see what it leads to.

When a substance decomposes in a reversible way and yields a larger number of molecules than compose the initial body, it is often said to *dissociate*. N_2O_4 dissociates, HI does not properly do so. We saw that pressure had no effect on the decomposition of HI; let us see how it is with N_2O_4. Substituting p for c in 108, we get for N_2O_4 the equilibrium equation

$$K = \frac{p'^2}{p}.$$

When p is changed n-fold,

$$K = \frac{(np')^2}{np} = \frac{np'^2}{p}.$$

As K is constant, and n likewise, p' and p must change, and therefore x likewise must change. This result is general. *Whenever the volume of the products is different from the volume of the initial bodies,* a change in p produces a change in x.

The decomposition of CO_2 is interesting. The reaction is

$$2\,CO_2 = O_2 + 2\,CO,$$

and so 108 becomes $$K = \frac{p_1' p_2'^2}{p^2},$$

where p_1' is the pressure of O, p_2' that of CO, and p that of CO_2. At equilibrium,

$$2\,CO_2 = 2(1-x)\,CO_2 + xO_2 + 2xCO.$$

If P is the total pressure, we have

$$p = \frac{2(1-x)}{2(1-x)+x+2x}P = \frac{2(1-x)}{2+x}P,\ p_1' = \frac{x}{2+x}P,\ p_2' = \frac{2x}{2+x}P,$$

and therefore,

$$K = \frac{x^3}{2(1+x)(1-x)^2}P.$$

At 3000° and 76 cm. Hg, x has been found to be $= 0.4$, and $K = 0.0741$. From these values we can find x for any pressure at 3000°. The following table gives x for many pressures and temperatures; pressures in atmospheres, 1 atmosphere $= 76$ cm. Hg.

$t°$	$P=0.001$	$P=0.01$	$P=0.1$	$P=1$	$P=10$	$P=100$
1000°	0.007	0.003	0.0013	0.0006	0.0002	0.00015
2000°	0.40	0.125	0.08	0.04	0.03	0.035
3000°	0.94	0.80	0.60	0.40	0.21	0.10
3500°	0.96	0.85	0.70	0.53	0.32	0.15
4000°	0.97	0.90	0.80	0.63	0.45	0.25

So, even at very high temperatures, a very appreciable quantity of CO_2 is still undecomposed.

Problem. — The effect of temperature comes out very plainly. What is it, and why?

Addition of an inert gas to a gaseous system in equilibrium should only disturb the equilibrium in so far as it alters the pressure or volume. When equilibrium is independent of volume, it should not be disturbed by adding an inert gas. For instance, addition of N to HI, in equilibrium with H and I,

should not disturb the system either when the total volume is increased to keep p constant or when v is kept constant and p increased. But when N is added to N_2O_4, in equilibrium with NO_2, the matter is different. For, in this case, equilibrium is dependent upon v or p. Experiment amply confirms these statements.

The addition, however, of any one of the reacting bodies to a system in equilibrium always disturbs the equilibrium, unless p is so adjusted as to just prevent the impending disturbance.

Consider a system whose equation of equilibrium is

$$K = \frac{p_1' p_2'}{p}. \qquad 118$$

Suppose we add one of the products of the reaction, say number 2. Then p_2' is increased by p_3'; but p_2' may decrease. To cover this possibility, let us put the total pressure of number $2 = p_2' - \pi + p_3'$. The total pressure of number 1 must then be $= p_1' - \pi$, and that of the initial body $= p + \pi$. So 108 becomes

$$K = \frac{(p_1' - \pi)(p_2' - \pi + p_3')}{p + \pi}. \qquad 119$$

Comparing 118 and 119, it is evident that they only agree when π is positive. If π were negative, the numerator of 119 would be greater than the numerator of 118, while the denominator of 119 would be less than the denominator of 118. So K of 118 and K of 119 would not have the same value, which they must have according to the law of equilibrium. Consequently, *the addition of one of the products of the decomposition to a gaseous system in equilibrium diminishes the decomposition.*

Problem.

Determine the effect of adding some of the *initial* body to a gaseous system in equilibrium.

65. **Equilibrium in liquid systems.** — We shall now proceed to apply 108 to liquid systems. That is, to bodies either liquid themselves or in solution. We have learned that liquids and solutions are to be treated like gases.

A favorite subject of study in this connection are the reactions between acids and bases. Not metallic bases, for then the reaction proceeds so far that one or more of the initial bodies disappear beyond detection; but the weak bases of the carbon compounds, the alcohols, and sometimes the alkaloids.

The general chemical equation is

$$zH_yR + yM(OH)_z = M_yR_z + zyH_2O$$

where M is any basic radical of a carbon compound, R any acid radical, y the valency of R, z the valency of M. Usually $y = z$ and not greater than 3. In this case

$$H_yR + M(OH)_y = (1-x)H_yR + (1-x)M(OH)_y + xMR + xyH_2O,$$

where x is the fraction of the grammolecule of H_yR and $M(OH)_y$ which react.

Consider the following case:

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O.$$

At equilibrium,

$$CH_3COOH + C_2H_5OH = (1-x)CH_3COOH + (1-x)C_2H_5OH + xCH_3COOC_2H_5 + xH_2O.$$

PROBLEMS.

1. With 1 grammolecule each of CH_3COOH and C_2H_5OH, $x = \frac{2}{3}$. What is K? *Ans.* 4.

2. With 1 grammolecule of CH_3COOH and a grammolecules of C_2H_5OH, what is x? *Ans.* $\frac{2}{3}(a+1-\sqrt{a_2-a+1})$.

3. With 1 grammolecule acetic acid, a grammolecules ethyl alcohol, and b grammolecules of water, what is x?

Ans. $\frac{1}{6}\{4(1+a)+b-\sqrt{16(a^2-a+1)+8(a+ab)+b^2}\}$.

There are some interesting cases of direct combination of carbon compounds corresponding to the action of ammonia. For example, pentylene C_5H_{10} and trichloracetic acid:—

$$C_5H_{10} + CCl_3COOH = CCl_3COOC_5H_{11}.$$

PROBLEMS.

1. 2.15 grammolecules C_5H_{10}, and 1 grammolecule CCl_3COOH in 361 cc., $x = 0.762$. What is K? *Ans.* 836.

2. 1 grammolecule CCl_3COOH, and a grammolecules C_5H_{10} in 638 cc., $x = 0.820$. What is a? *Ans.* 4.3.

3. 1 grammolecule of CCl_3COOH, and 9.1 grammolecules C_5H_{10}, $x = 0.86$. What is v? *Ans.* 1119 cc.

4. Suppose x in problem 3 is unknown, calculate it with known v.

Suppose we have a body A, which combines with two other bodies, B and C, and in solution 1 gramequivalent of A and 1 grammolecule each of B and C. A *gramequivalent* of a body is a quantity equal to 1 gramvalency; that is, equal to 1 grammolecule divided by the valency of the molecule. The body A divides between B and C according to the equation,

$$aA + bB + cC = y_1AB + (a - y_1)\,AC + (b - y_1)\,B + \{c - (a - y_1)\}\,C.$$

The chemical reaction is

$$AC + B = AB + C,$$

and at equilibrium,

$$K_1 = \frac{\{c - (a - y_1)\}y_1}{(a - y_1)(b - y_1)}. \qquad 120$$

Similarly when D is substituted for C,

$$AB + D = AD + B,$$

and

$$K_2 = \frac{\{b - (a - y_2)\}y_2}{(a - y_2)(d - y_2)}. \qquad 121$$

Multiplying

$$K_1K_2 = \frac{\{c-(a-y_1)\}\,y_1\,\{b-(a-y_2)\}\,y_2}{(a-y_1)\,(b-y_1)\,(a-y_2)\,(d-y_2)}. \qquad 122$$

This condition of equilibrium corresponds to the chemical reaction.

$AC + B + AB + D = C + AB + B + AD$ or $AC + D = AD + C$,

so the *product of the equilibrium constant of B on AC into the equilibrium constant of D on AB equals the equilibrium constant of D on AC.* For as AB and B are in equal amounts as initial bodies and products, they do not affect the action of D on AC nor of A on CD, and finally disappear.

This conclusion has been tested experimentally, and found to hold good.

In a similar way we can find the division of an acid between two bases or of a base between two acids.

For reasons that shall appear later, all salts, bases, and acids are supposed to be more or less decomposed in a peculiar way in aqueous solutions. They are supposed to be *ionized.* This term need not be explained except to say that the equations of ionization for the bodies considered are

$$M_1OH = M_1 + OH, \qquad a$$

$$M_2OH = M_2 + OH, \qquad b$$

$$M_1R = M_1 + R, \qquad c$$

$$M_2R = M_2 + R. \qquad d$$

We assume that M_1, M_2, R are monovalent. Let

x_1 = degree of ionisation of M_1OH,

x_2 = degree of ionisation of M_2OH,

y_1 = degree of ionisation of M_1R,

y_2 = degree of ionisation of M_2R,

q_1 = quantity of M_1OH reacting with HR,

$q_2 = 1 - q_1$ quantity of M_2OH reacting with HR.

The quantity q_1 consists of two parts, a part as $M_1R = q_1(1 - y_1)$ and a part as $M_1 + R = q_1y_1$; similarly for q_2 we have

$$q_2(1 - y_2) = (1 - q_1)(1 - y_2) \text{ and } q_2y_2 = (1 - q_1)y_2.$$

A part of the M_1OH not acted on by HR is ionized according to a. This part $= (1 - q_1)x_1$. Similarly for M_2OH we have the ionized part $= (1 - q_2)x_2 = q_1x_2$.

Collecting, we get for the total quantities

of $M_1R = q_1(1 - y_1)$; of $M_2R = (1 - q_1)(1 - y_2)$;

of $M_1OH = (1 - q_1)(1 - x_1)$; of $M_2OH = q_1(1 - x_2)$;

of $M_1 = q_1y_1 + (1 - q_1)x_1$; of $M_2 = (1 - q_1)y_2 + q_1x_2$;

of $R = q_1y_1 + (1 - q_1)y_2$; of $OH = (1 - q_1)x_1 + q_1x_2$.

Hence the conditions of equilibrium for a, b, c, d, are respectively,

$$K_1 = \frac{[q_1y_1 + (1 - q_1)x_1][q_1x_2 + (1 - q_1)x_1]}{(1 - q_1)(1 - x_1)v}, \qquad e$$

$$K_2 = \frac{[(1 - q_1)y_2 + q_1x_2][(1 - q_1)x_1 + q_1x_2]}{q_1(1 - x_2)v}, \qquad f$$

$$K_3 = \frac{[q_1y_1 + (1 - q_1)x_1][q_1y_1 + (1 - q_1)y_2]}{q_1(1 - y_1)v}, \qquad g$$

$$K_4 = \frac{[(1 - q_1)y_2 + q_1x_2][q_1y_1 + (1 - q_1)y_2]}{(1 - q_1)(1 - y_2)v}. \qquad h$$

Dividing e by f,

$$\frac{K_1}{K_2} = \frac{[q_1y_1 + (1 - q_1)x_1](1 - x_2)q_1}{[(1 - q_1)y_2 + q_1x_2](1 - q_1)(1 - x_1)}. \qquad i$$

Salts of the type MR, where M and R are monovalent, M being a metal, are largely and equally ionized in aqueous solution, each salt considered separately; so for any salt MR,

$$K_1 = K_2 = K_3 = K_4 \ldots$$

When the salts are in a solution together we may make the same assumption.

Hence
$$\frac{q_1y_1 + (1 - q_1)x_1}{(1 - q_1)y_2 + q_1x_2} = \frac{q_1(1 - y_1)}{(1 - q_1)(1 - y_2)}. \qquad j$$

Substituting in *i*,

$$\frac{K_1}{K_2}=\frac{q_1(1-y_1)}{(1-q_1)(1-y_2)}\cdot\frac{(1-x_2)q_1}{(1-q_1)(1-x_1)}=\left(\frac{q_1}{1-q_1}\right)^2\left(\frac{1-y_1}{1-y_2}\right)\left(\frac{1-x_2}{1-x_1}\right). \quad 123$$

In the case of the monovalent salts under consideration, $y_1 = y_2$. For weak bases like alcohols, x_1 and x_2 are very small in comparison with 1. In this particular case, viz. for weak bases, therefore, 123 reduces to

$$\frac{K_1}{K_2}=\left(\frac{q_1}{1-q_1}\right)^2 \text{ or } \frac{q_1}{1-q_1}=\sqrt{\frac{K_1}{K_2}}. \quad 124$$

That is, *the partition of an acid between two weak bases is approximately proportional to the square roots of the ionisation constants of these bases.*

From *a* and *b*,

$$K_1=\frac{x_1^2}{(1-x_1)v},\quad K_2=\frac{x_2^2}{(1-x_2)v},$$

and hence for weak bases,

$$\frac{K_1}{K_2}=\frac{x_1^2}{1-x_1}\cdot\frac{1-x_2}{x_2^2}=\frac{x_1^2}{x_2^2}.$$

With 124,

$$\frac{q_1}{1-q_1}=\frac{x_1}{x_2}. \quad 125$$

That is, *the partition of an acid between two weak bases is approximately proportional to the degrees of ionisation of the bases.*

On changing M_1OH and M_2OH into HR_1 and HR_2, and HR into MOH, we get corresponding rules for the partition of a base between two weak acids.

When the solvent is not one of the reacting bodies, it is neglected in considering the equations of the system; when the solvent is one of the reacting bodies, it cannot be neglected. Consider the reaction of acetic acid and alcohol in an aqueous solution. The chemical reaction is

$$CH_3COOH + C_2H_5OH + aH_2O = CH_3COOC_2H_5 + (a+1)H_2O,$$

and, at equilibrium,

$$CH_3COOH + C_2H_5OH + aH_2O = (1-x)CH_3COOH + (1-x)C_2H_5OH + xCH_3COOC_2H_5 + (a+x)H_2O.$$

The equation of equilibrium is

$$K = \frac{x(a+x)}{(1-x)^2} = \frac{x}{(1-x)^2}; \qquad 126$$

for, when a is very large, x vanishes in comparison with it, and therefore $a + x$ is a constant nearly, and may be absorbed in K, giving the second value of 126. So, when the solutions are dilute, the solvent is to be treated as a constant quantity; when concentrated, the solvent is treated as one of the reacting bodies. Whether the system belongs to the dilute or concentrated state may be determined by comparing x and a.

66. **Equilibrium in solid systems.** — Very little has been done with such systems, either theoretically or experimentally. The work in this line has been confined to mixed or composite crystals.

67. **Equilibrium in solid-gas systems.** — In these cases, the equilibrium equation assumes a very simple form. Experience has shown that *so long as each of the reacting solids is present*, each behaves as if its concentration were constant, and therefore all the concentrations of the solids may be included in K. The concentrations of the *gases* therefore determine the equilibrium. For example,

$$CaCO_3 = CaO + CO_2,$$

$$CaCO_3 = (1-x)CaCO_3 + xCaO + xCO_2.$$

As CO_2 is the only gas, at equilibrium,

$$K = c = \frac{x}{v} = p, \qquad 127$$

where p is the pressure of CO_2 in the system at equilibrium. Consequently, at constant temperature, equilibrium is determined by the concentration or pressure of the CO_2 only, no matter how much $CaCO_3$ or CaO is present.

There are two explanations for this:

(1) The solids are supposed to give off vapor of the same composition as themselves, too small in quantity to be directly detected, but enough to react with other gases or vapors. So at a fixed temperature, so long as any solid is present, the concentration of the vapor of that particular solid is constant.

(2) Gases and vapors are so mobile compared with solids, that, so long as any appreciable quantities of the latter are present, every particle of the gases will come in contact with the solids in a short time; so that increasing the quantity of solid does not materially increase the opportunity of a gas to react with it.

It is hard to say which explanation is to be preferred. Perhaps the first is.

Problems.

1. Solid ammonium hydrosulfid decomposes thus at 25.1°,

$$NH_4SH = H_2S + NH_3.$$

$K = 62400$, pressure of $H_2S = 294$ mm. Hg. What is the pressure of NH_3? *Ans.* 212 mm. Hg.

2. Pressure of $NH_3 = 417$ mm. Hg. What is the pressure of H_2S? *Ans.* 150 mm. Hg.

3. Iron and water react thus at 440°,

$$3\,Fe + 4\,H_2O = Fe_3O_4 + 4\,H_2.$$

What is the equilibrium equation? Why? *Ans.* $K = \left(\frac{c'}{c}\right)^4$.

4. When the pressure of H_2O vapor in $3 = 4.6$ mm. Hg, then pressure of $H_2 = 10.1$ mm. Hg. When H_2 has pressure $= 60$ mm. Hg, what is the pressure of H_2O vapor? Why?

Ans. 27.3 mm. Hg.

68. **Equilibrium in liquid-gas systems.** — When the gaseous part is the vapor of the liquid, the equilibrium equation is very simple. Experience has shown that the concentration of the vapor, so long as liquid is present, is determined only by the temperature, not at all by the quantity of the liquid, provided there is enough of the liquid for some to remain over after the available space has been filled with vapor. So

$$K = c = \frac{x}{v} = p. \qquad 128$$

When the gaseous part comes from a substance in solution, and the solvent does not give off vapor, we have as the condition of equilibrium

$$K = \frac{c'}{c} = \frac{p}{\pi}, \qquad 129$$

where c' is the concentration of the gas, and p its pressure in the gaseous part, while c and π are the corresponding quantities in the solution.

Equation 129 is the analytical expression of Henry's law.

Sometimes, indeed often, the molecular weight of a body in the gaseous state is not the same as its molecular weight in solution. In such cases let

$$A_z = zA, \qquad 130$$

and, therefore, from 108,

$$K = \frac{(c')^z}{c}. \qquad 131$$

When the system contains more than one body in the gaseous state and more than one in the liquid state, there is a separate equation like 129 for each body.

Consider a solution of acetic acid in benzene. A molecular weight determination by freezing shows that acetic acid in benzene is in two molecular states, $(CH_3COOH)_2$ and CH_3COOH. Therefore, the chemical equation is

$$(CH_3COOH)_2 = 2\,CH_3COOH. \qquad a$$

At equilibrium,

$$(CH_3COOH)_2 = (1-x)(CH_3COOH)_2 + 2xCH_3COOH. \qquad b$$

The equilibrium equation is

$$K = \frac{(c')^2}{c} = \frac{(2x)^2}{(1-x)v}. \qquad 132$$

When 0.663 grams acetic acid are dissolved in 100 grams benzene, 10% of acid is decomposed into simple molecules. Hence, supposing the volume is constant throughout the discussion and is absorbed in K,

$$K = \frac{(2 \cdot 0.663 \cdot 0.1)^2}{0.663 \cdot 0.9} = 0.0295, \qquad 133$$

and, therefore,

$$\frac{w(2x)^2}{1-x} = 0.0295, \qquad 134$$

where w is the quantity of acetic acid in grams dissolved in 100 grams benzene, and x is the degree of decomposition of the $(CH_3COOH)_2$ molecules. So x can be calculated for any w from 134.

Since acetic acid decomposes into simpler molecules when dissolved in benzene, we must put

$$n = \frac{w(1+x)}{120}.$$

So from 78,

$$p_1 = p_0 - p_0 \frac{\frac{[w(1+x)]}{120}}{\frac{100}{78} + \frac{[w(1+x)]}{120}}, \qquad 135$$

where 78 is the assumed molecular weight of benzene. At 80°, vapor tension of benzene is 750 mm. Hg $= p_0$, and from 135 we can calculate the vapor pressure of the solution, *provided the acetic acid does not give off vapor.* But it evidently does give off vapor; for when we heat a solution in which $w = 1.87$ grams we find that the vapor pressure of 750 mm. Hg is reached at a

temperature 0.155° below 80°. Now, at this temperature, if P is the vapor pressure of the acetic acid and $x = 0.06$ from 134, we have, with 135,

$$P = 750 - p_1 = 750 - p_0 \frac{\frac{100}{78}}{\frac{100}{78} + \frac{1.87 \cdot 1.06}{120}}.$$

But at this lower temperature p_0 is not equal to 750 mm. Hg, but equal to $750 - at$, where a is the change in vapor pressure due to change of 1°. This quantity can be calculated from 50, and in this case is 22.2 mm. Hg. So

$$P = 750 - (750 - 22.2 \cdot 0.155°) \frac{\frac{100}{78}}{\frac{100}{78} + \frac{1.87 \cdot 1.06}{120}} = 13 \text{ mm. Hg.}$$

That is, in a mixture of the given composition the pressure of the acetic acid in the vapor is 13 mm. Hg.

Problems.

1. When 4.13 grams acetic acid are dissolved in 100 grams benzene, what is x? *Ans.* 0.04.

2. When 6.83 grams acetic acid are dissolved in 100 grams benzene, change in boiling point of solution $= + 0.063°$. What is P? *Ans.* 31.5 mm. Hg.

The reader should notice that the molecular weight of benzene is taken as 78, its normal value. This is by no means assured, but by assuming this value we get such excellent agreement between theory and fact that for the present, at any rate, this value must be accepted. This will appear evident from the following.

From 134, $$x = \sqrt{\frac{0.0295\,(1-x)}{4\,w}}.$$

So for w grams of acetic acid in solution,

$$wx = \frac{\sqrt{0.0295\,(1-x)w}}{2}. \qquad 136$$

For the vapor of acetic acid, from 117,

$$x' = \frac{\partial - \Delta}{\Delta} = \frac{4.146 - \Delta}{\Delta}, \qquad 137$$

where x' is the number of grammolecules of CH_3COOH, ∂ the normal density compared with air of the $(CH_3COOH)_2$ molecules $= 4.146$, and Δ the observed density. This has been very carefully determined, and is given by the equation

$$l_{10}\frac{2.073\,(\Delta - 2.073)}{(4.146-\Delta)^2 P} = \frac{3520}{T} - 11.349.$$

At the boiling point of benzene, $T = 353°$ so that

$$\frac{\Delta - 2.073}{(4.146-\Delta)^2 P} = 0.0203. \qquad 138$$

For the concentration given in the second problem on page 105 we have $P = 31.5$, and so $\Delta = 2.94$. With these values we can find x'. The following table gives some of these values:

w	Δt	x	P	Δ	x'	K_1
0.150	− 0.070	0.20	2.4	2.24	0.87	91.8
0.663	− 0.139	0.10	6.6	2.44	0.70	82.5
1.64	− 0.152	0.065	11.8	2.61	0.60	81.3
2.60	− 0.132	0.055	16.1	2.71	0.54	81.3
5.00	+ 0.032	0.038	23.6	2.83	0.47	81.8
8.42	+ 0.180	0.029	36.4	3.02	0.36	81.1

In the table Δt is the change in boiling point produced by w grams acetic acid in 100 grams of solvent.

The concentration of the CH_3COOH molecules in the vapor is given by the equation

$$\Delta \cdot P\frac{\partial - \Delta}{\Delta} = P(4.146 - \Delta). \qquad 139$$

So if Henry's law is true, we should have the relation,

$$P(4.146 - \Delta) = K_1\sqrt{0.0295\, w(1 - x)}, \qquad 140$$

where K_1 is a new constant. That K_1 is a constant is evident from the above table.

It is this excellent agreement between theory and observation that justifies us in assuming that the molecular weight of benzene when used as a solvent is 78.

There are other systems of a similar nature, but we cannot consider them. The student should verify the table above, until he is thoroughly conversant with it.

69. **Equilibrium in solid-liquid systems.** — The principle that shall guide us in the study of saturated solutions is this: A solid in contact with its saturated solution behaves like a solid in a space saturated with its vapor. We should not forget, however, that in the vapor state the available volume is very great compared with the volume of the particles, but in a liquid state the available volume is very small compared with the volume of the particles. Or in other words the concentration of the volume energy in the vapor state is small, in the liquid state it is great, in each case for equal molecular quantities.

When we bring a solid in contact with a liquid, the solid generally passes into solution, and continues doing so until the osmotic pressure of the solute prevents further solution, and the solution is said to be saturated. At least, this is the way we shall look at the matter. The quantity of solid which dissolves varies with the temperature and nature of solid and solvent. No general law has yet been discovered. We have good reason for thinking that all bodies are soluble in all solvents, though often so slightly that we cannot get direct

evidence of solution having taken place. The best evidence in the case of metals is of electrical nature, and will be described later. When a saturated solution of a body, whose solubility increases with T, is cooled in a carefully protected tube, the body does not always separate, though, starting with pure solvent at this temperature, it is not possible to dissolve so much solid as it contained when proceeding in the first way. The moment, however, we introduce a most minute quantity of solid into the solution, a part of the solid separates; and when the separation has ceased, the solution has the same composition it would have had if we had started from pure solvent and solid. The temperature is supposed to be the same in each case, of course. So we see that the quantity of solid that will dissolve is often dependent upon the presence of the solid while making the solution. Sometimes a solid different from the solute will cause the separation, but this solid and the solute must be isomorphous. A solution that contains more solute than it will dissolve in the presence of solid solute is said to be *supersaturated*. We cannot make supersaturated solutions with every solvent and every solute. Whether this is due to the nature of solvent and solute or to the conditions not being right must be left to the future to decide.

When we admit an inert gas into a space saturated with moisture, none of the latter separates, if the admission be conducted properly, unless the pressure becomes very great. So when a second solid is added to a saturated solution, we might expect just so much of the second solid to dissolve as if no other body were present, and expect none of the first solid to separate at all. But whereas in the case of the gas the pressure is generally small, for the available space is large, in the case of the solution the osmotic pressure is generally very great, for the available space is small. So the behavior is only in a general way a guide, and the presence of one body may affect the solubility of another.

If a solid or liquid A is soluble in a solvent S_1, and both A

and S_1 are more or less readily soluble in solvent S_2, then the addition of some S_1 to a saturated solution of A in S_2 will presumably not cause separation of A. For, as A is soluble in S_1, the osmotic pressure of A in $S_2 + S_1$ is not changed much, if at all, unless large quantities of S_1 are added. In that case the system becomes one in which S_1 is the solvent, and then whether A separates or not depends upon its relative solubility in S_2 and S_1.

Many metallic salts are only slightly soluble in alcohol. When alcohol is added to saturated aqueous solutions of such salts, a precipitate of the salt is produced.

On the other hand, carbon compounds are generally largely soluble in alcohol, particularly those which also dissolve in water. So, when alcohol is added to such aqueous saturated solutions, the solute does not precipitate.

Many substances, on dissolving, decompose in a molecular way; the polymeric molecule breaks down into simpler molecules, as illustrated by equation 130, A_z being the polymeric molecule. This is particularly the case when water is the solvent. We have had an example of the decomposing action of water in § 65, which, however, is not a polymeric decomposition such as we are now considering. Of course we may claim that the natural molecular weight is the simplest, as it is in aqueous solution, and that other solvents like benzene, alcohol, polymerize the molecule. It makes little difference which view we accept. Substances also decompose in a way corresponding to that of phenanthrene picrate, which we shall examine in detail. In alcoholic solution this salt decomposes into phenanthrene and picric acid, according to the equation

$$C_{14}H_{10}.C_6H_2(NO_2)_3OH = C_{14}H_{10} + C_6H_2(NO_2)_3OH.$$

So, from 108, $$K = \frac{c_1' c_2'}{c}, \qquad 141$$

where c_1' is the concentration of phenanthren, c_2' that of picric acid, and c, of course, that of phenanthren picrate. Since we

use saturated solutions, and of course temperature is constant, c is constant, and 141 reduces to

$$K_1 = c_1' c_2'. \qquad 142$$

We can determine c by dissolving phenanthren picrate in a saturated alcoholic solution of either picric acid or phenanthren, for in such solutions phenanthren picrate should not decompose.

At 12.3°, $c = 0.173$ grams in 100 grams solution; at 17.5°, $c = 0.220$ grams in 100 grams solution.

In the following problems the solution is to be supposed saturated with phenanthren picrate.

Problems.

1. $K_1 = 0.516$, $c_1' = 2.007$ grams in 100 grams of solution, temperature = 12.3°. What is c_2'?

Ans. $c_2' = 0.258$ in 100 grams solution.

2. 2.141 grams phenanthren and 0.409 grams picric acid are dissolved in 100 grams of *pure* alcohol. Phenanthren picrate is therefore formed in the solution. Temperature = 12.3°. What is K_1? *Ans.* 0.656.

But in the first problem K_1 was given as 0.516. Hence, either our theory is wrong or some assumption is made that is not in harmony with fact. The trouble is probably in the assumed composition of phenanthren and picric acid in the alcohol solution. We examine each body separately in alcohol solution by a vapor-pressure determination, or by a boiling-point determination. We find that picric acid in alcohol has the normal formula $C_6H_2OH(NO_2)_3$, but that phenanthren seems to be polymerized into the triple molecule $(C_{14}H_{10})_3$, not entirely, for there are molecules $C_{14}H_{10}$, but largely, so that a considerable part of the 2.141 grams is in the form $(C_{14}H_{10})_3$. This part presumably cannot react with picric acid, and must be subtracted from the total quantity of phenanthren present.

To do this, we need the equilibrium equation for phenanthren. The reaction is

$$(C_{14}H_{10})_3 = 3C_{14}H_{10},$$

and so

$$K_2 = \frac{(c_1')^3}{c_3} = 10.36, \qquad 143$$

from a boiling-point determination. In the problem in question we must subtract from 2.141 the quantity of phenanthren as phenanthren picrate in solution; namely, $0.173 \cdot 178/407$, and the balance, $2.141 - 0.173 \cdot 178/407 = 2.044$ grams, is the phenanthren. The triple molecules, c_3, are $2.044 - c_1'$. Substituting in 143,

$$10.36 = \frac{(c_1')^3}{2.044 - c_1'},$$

or

$$c_1' = 1.62.$$

This value substituted in 142 gives

$$K_1 = 0.505$$

as the corrected answer to problem 2.

The student should work out several such problems from the following table:

$t°$.	Picric Acid.	Phenanthren.	Picrate $= c$.	K_1.	K_2.
12.3	0.534	1.413	0.173	0.516	10.36
17.5	1.051	0.817	0.220	0.635	10.36
17.5	1.285	0.682	0.220	0.635	10.36
17.5	6.150	0.195	0.220	0.635	10.36

Under picric acid and phenanthren are given the *total* quantities added to the solvent, and, consequently, to get c_1' and c_2' the quantities needed to form phenanthren picrate must be subtracted.

When we add to a saturated solution of a body which decomposes on solution one of the products of the decomposition,

a part of the dissolved body should precipitate, for from 119 we see that a decomposition is diminished by adding one of the products of decomposition, and as the solution was previously saturated, the part that is re-formed must separate. From a few fundamental data we can calculate in many cases very accurately the quantity precipitated.

Let us consider a saturated aqueous solution of a metallic salt. As we have already seen in § 64, salts ionize or decompose thus

$$aM_xR_y = M_{x-1}R_y + M_{x-2}R_y + \cdots + MR_y + M_xR_{y-1} + \cdots + M_xR + M_{x\ 1}R_{y\ 1} + \cdots + MR + xM + yR \qquad 144$$

where M is the metallic radical, and R, the acid radical.

We must select a salt not very soluble, for the solution must be saturated and yet not concentrated, for then there are too many complications. Let the salt be silver bromate. We have $a = x = y = 1$, and so 144 becomes

$$AgBrO_3 = Ag + BrO_3. \qquad 145$$

The equation of equilibrium is

$$K = \frac{c_1'c_2'}{c} = \frac{(w_0x_0)^2}{w_0(1 - x_0)}, \qquad 146$$

where c refers to $AgBrO_3$, c_1', c_2' to Ag and BrO_3 respectively, x_0 is the degree of decomposition or ionisation, and w_0 the quantity of $AgBrO_3$ dissolved. On adding Ag, not, of course, as metallic silver, but in the same form as in 145, as silver nitrate or as silver sulphate, for all silver salts decompose in the same way as $AgBrO_3$ does, w_0 is diminished. Let the new solubility be w_1, and let x_1 be the degree of decomposition under the new conditions, and let c_3 be the concentration of the Ag from the silver nitrate or sulphate, or from whatever the second salt of silver may be. Equation 146 becomes

$$K = \frac{w_1x_1(w_1x_1 + c_3)}{w_1(1 - x_1)}. \qquad 147$$

From the fundamental conception of the analogy of solutions to gases, and from the fact that in each case the solution is saturated with $AgBrO_3$, we claim that

$$w_0(1 - x_o) = w_1(1 - x_1). \qquad 148$$

Eliminating K,

$$w_1 = -\frac{c_3}{2x_1} + \sqrt{w_0^2\left(\frac{x_0}{x_1}\right)^2 + \left(\frac{c_3}{2x_1}\right)^2}. \qquad 149$$

Problems.

1. For $AgBrO_3$, $w_0 = 0.00810$ grammolecules in 1000 cc. solution. $c_3 = 0.00850$ grammolecules in 1000 cc. of $AgNO_3$ solution. What is w_1? In such dilute solution consider $x_0 = x_1 = 1$.

Ans. 0.00489 in what units?

2. $AgBrO_3$ of same concentration, and $KBrO_3$ for which $c_3 = 0.0346$ grammolecules in 1000 cc. solution. What is w_1? Consider $x_0 = x_1 = 1$. *Ans.* 0.0018 in what units?

3. With thallium chlorid, TlCl, as initial body and NH_4Cl as precipitant, $w_0 = 0.01612$ grammolecules in 1000 cc. solution, $c_3 = 0.025$ grammolecules in 1000 cc. solution, $x_0 = x_1 = 1$. What is w_1? *Ans.* 0.00789 in what units?

4. $$CaCl_2 = Ca + 2\,Cl.$$

Use this as a precipitant in No. 3 instead of NH_4Cl. $x_0 = 1$, but $x_1 = 0.82$, $c_3 = 0.0344$ grammolecules in 1000 cc. solution. What is w_1? *Ans.* 0.0065 in what units?

5. Need the solution be saturated with the precipitant in these examples? Why?

6. When silver is determined by titration with a chlorid, it is found that after the chlorid is added in sufficient quantity by calculation to form AgCl with all the Ag, a further addition of the chlorid still shows the presence of Ag. When enough chlorid is added to precipitate all the Ag, and then a silver salt is added, the presence of Cl in the liquid is shown. This

can be precipitated by a silver salt again, and in turn the Ag precipitated by a chlorid, and so on.

AgCl is slightly soluble in water, 100 cc. dissolving about $0.0_5 25$ grammolecules AgCl. AgBr and AgI are far less soluble than this, and silver salts do not show this peculiar action with bromids and iodids.

Explain all this.

It is evident that when w_1 is known we can reverse matters and compute x_0 or x_1. This is a valuable means of determining degrees of decomposition or of ionisation.

We shall now pass to very interesting but complicated cases of carbon acids and salts in aqueous solution. The method can be applied to any set of bodies in any solvent.

Suppose we have a sodium salt in aqueous solution, and wish to determine how much of the acid of the sodium salt is precipitated by a given quantity of hydrochloric acid. This presupposes, of course, that the acid is only slightly soluble in water, so acetates, formates, oxalates, etc., cannot be used.

We have seen, § 64, that acids like salts ionize or decompose in aqueous solution. Accordingly at equilibrium,

$$HR = (1 - x)\,HR + xH + xR, \qquad 150$$

and

$$K = \frac{c_1' c_2'}{c_1}. \qquad 151$$

For a saturated solution c_1 is constant, and

$$K_0 = c_1' c_2'. \qquad 152$$

On adding HCl, we add one of the products of the ionic decomposition, and so some of the acid is precipitated.

Let R be the total quantity of acid radical in the system, c_1 the quantity of undecomposed carbon acid, and c_0 the quantity of precipitated carbon acid, all in grammolecules. Then the quantity remaining *in solution* as decomposed carbon acid or as ionized carbon acid is $R - c_1 - c_0$. Let H be the total

quantity of hydrogen. The quantity remaining in solution as ionized H is $H - c_1 - c_0$. From 152,

$$R_0 = (R - c_1 - c_0)(H - c_1 - c_0), \qquad 153$$

or
$$c_0 = \frac{H - 2c_1 + R}{2} - \tfrac{1}{2}\sqrt{4K_0 + (H - R)^2}. \qquad 154$$

Example. — 0.0025 grammolecules of sodium *o*-iodbenzoate are dissolved in water, 0.001 grammolecules hydrochloric acid added, and the whole made up to 135 cc. How much *o*-iodbenzoic acid is precipitated?

This solution is so dilute that we are to consider the HCl and the $C_6H_4ICO_2Na$ completely ionized, the latter into $C_6H_4ICO_2$ and Na. By some appropriate method, boiling-point determination, or freezing-point determination, or by some other method, we find that in 1000 cc. saturated aqueous solution of $C_6H_4ICO_2H$, $c_1' = c_2' = 0.00169$ grammolecules and $c_1 = 0.00215$ grammolecules. Therefore, from 152,

$$K_0 = (0.00169 \cdot 0.135)^2 = 0.0_752,$$
$$c_1 = 0.00215 \cdot 0.135 = 0.0_3290,$$
$$H = 0.001, \text{ and } R = 0.0025.$$

So, $c_0 = 0.0068$ grammolecules.

Problems.

1. 0.0025 grammolecules *o*-iodbenzoic acid, 0.0025 grammolecules NaOH, 0.0025 grammolecules HCl, made up to 135 cc. with water. What is c_0? *Ans.* 0.00198 grammolecules.

2. For cinnamic acid, in 1000 cc. solution $c_1' = c_2' = 0.0_3326$, $c_1 = 0.002993$. Solution of same strength as in 1 and like it. What is c_0? *Ans.* 0.00205 grammolecules.

3. A solution of sodium *p*-toluate of same strength as in 1. One grammolecule of *p*-toluic acid requires 394 liters H_2O for solution, degree of decomposition is 0.1326. What is c_0? *Ans.* 0.00126.

We shall now proceed to the separation of two acids. Let the primes refer to the first acid, the seconds to the second acid. We have as the general form of the equilibrium equations:

$$(R' - c_1' - c_0')(H - c_1' - c_1'' - c_0' - c_0'') = K'c', \qquad 155$$

$$(R'' - c_1'' - c_0'')(H - c_1' - c_1'' - c_0' - c_0'') = K''c''. \qquad 156$$

So soon as the liquid is saturated with acid, c' and c'' become constant. Before saturation and up to it, c_0' and $c_0'' = 0$.

Example. — 0.0025 grammolecules *o*-iodbenzoic acid, 0.0025 grammolecules cinnamic acid, 0.0050 grammolecules NaOH, and 0.0025 grammolecules HCl, are made up to 135 cc. with H_2O. What is c_0''? Only the second acid precipitates, so 155 reduces to

$$(R' - c_1')(H - c_1' - c_1'' - c_0'') = K'c_1', \qquad 157$$

and 156 to $(R'' - c_1'' - c_0'')(H - c_1' - c_1'' - c_0'') = K_0''$. 158

$K' = 0.00132$ by boiling-point determination or otherwise, $K_0'' = (0.0_3326 \cdot 0.135)^2$, $c_1'' = 0.002993 \cdot 0.135$. Substituting in 157 and 158 and eliminating c_1', we get $c_0'' = 0.0019$ grammolecules.

In a similar way we can determine the quantity of any acid precipitated from a mixture of three or more acids when certain fundamental data are given. But the algebraic operations are so tedious, even in the simple case of only two acids, that we shall not consider the mixture of three acids.

Since K gives the ratio of ionized parts of an acid to unionized part, and as the ionized parts are always soluble, that acid will be more soluble which has the larger K, the acids being supposed to have the same valency.

Problems.

1. An aqueous solution of *m*-brombenzoic acid, *o*-toluic acid, and NaOH of same strength as in example but *without* HCl. What is c_0'? The first acid separates. $K_0' = (0.0_346 \cdot 0.135)^2$, $K'' = 0.0_312$, $c_1' = 0.001542 \cdot 0.135$. *Ans.* 0.0016 grammolecules.

2. An aqueous solution of *o*-iodbenzoic acid and *p*-toluic acid of same strength, as in example, but with 0.0025 grammolecules of NaOH instead of 0.0050 grammolecules. What is c_0''? *p*-toluic acid separates.

$K' = 0.00132$, $K_0'' = (0.0_3337 \cdot 0.135)^2$, $c_1'' = 0.002203 \cdot 0.135$.

Ans. 0.0020 grammolecules.

When both acids precipitate, we have the equations

$$(R' - c_1' - c_0')(H - c_1' - c_1'' - c_0' - c_0'') = K_0', \qquad 159$$

$$(R'' - c_1'' - c_0'')(H - c_1' - c_1'' - c_0' - c_0'') = K_0''. \qquad 160$$

EXAMPLE. — 0.0025 grammolecules *o*-iodbenzoic acid, 0.0025 grammolecules *p*-toluic acid, 0.005 grammolecules NaOH, and 0.003 grammolecules HCl, are made up to 135 cc. with H_2O. What are c_0' and c_0''? $K_0' = (0.001686 \cdot 0.135)^2$, $K_0'' = (0.0_3337 \cdot 0.135)^2$, $c_1' = 0.002152 \cdot 0.135$, $c_1'' = 0.0022 \cdot 0.135$. Dividing 159 by 160,

$$\frac{R' - c_1' - c_0'}{R'' - c_1'' - c_0''} = \frac{K_0'}{K_0''},$$

which, with either 159 or 160, gives c_0''. Both K_0' and K_0'' are so small that we can put them equal to zero and thereby simplify the calculation. We find $c_0' = 0.045$, $c_0'' = 0.303$, both in grams.

PROBLEMS.

1. An aqueous solution of 0.0025 grammolecules each of *o*-iodbenzoic acid and cinnamic acid, 0.005 grammolecules NaOH, and 0.005 grammolecules HCl. What are c_0' and c_0''? Degree of decomposition of cinnamic acid is 0.0982 when solution is saturated. Solubility of cinnamic acid is 0.4911 grams in 1000 cc. H_2O.

Ans. $c_0' = 0.491$, $c_0'' = 0.304$, both in what units?

2. Answer same question for *m*-iodbenzoic acid and anisic acid. Degree of decomposition of *m*-iodbenzoic is 0.4408, of anisic acid, 0.1363 at saturation. Solubility of *m*-iodbenzoic is 0.1163 grams in 1000 cc. H_2O, of anisic acid, 0.2263 grains in 1000 cc. H_2O. *Ans.* $c_0' = 0.297$, $c_0'' = 0.166$ in what units?

We now proceed to determine how to separate two acids by fractional precipitation. We first find the values of K_0' and K_0'', that is, the product of the ionized parts. As the acid for which K_0 is the greater is the more soluble, on adding the precipitant, HCl, HNO_3, etc., the acid with smaller value of K_0 precipitates first. We therefore make the c_0 which corresponds to the larger K_0 equal to zero, and then, substituting the given quantities in 159 and 160, solve for H. This gives the quantity of H needed to just not precipitate one of the acids and to partly precipitate the other.

Example. — Suppose we have 0.0025 grammolecules of *o*-iodbenzoic acid, 0.0025 grammolecules *p*-toluic acid, 0.005 grammolecules NaOH, and we wish to determine how much HCl should be added so that, on making up the solution to 135 cc. with H_2O, the maximum quantity of *p*-toluic acid is separated, for $K_0' > K_0''$.

$$K_0' = (0.00169 \cdot 0.135)^2,$$
$$K_0'' = (0.0_3337 \cdot 0.135)^2,$$
$$c_1' = 0.002152 \cdot 0.135,$$
$$c_1'' = 0.002203,$$
$$c_0' = 0,$$
$$R' = R'' = 0.0025.$$

Substituting in 159 and 160, we get $H = 0.0027$ grammolecules and $c_0'' = 0.0021$ grammolecules.

The solution is now made up to any desired volume, say 200 cc. The HCl necessary for a second precipitation is found by putting $c_0'' = 0$ and calculating c_0', remembering that now

$R'' = 0.0025 - 0.0021 = 0.0_34$, and that instead of 135 cc. we have 200 cc.

We proceed in a similar way for any number of acids.

We have considered in a general way the relation of solvent and solute. There is now a definiteness of treatment which the subject never had before, and although far from being finished, although we are far from being able to state everything that occurs, and constantly meeting apparently contradictory facts, we may feel sure that in the main we are working in the right direction, and that the difficulties will be explained in time and found to harmonize with our present ideas of solution.

70. **Partition of a substance between two solvents.** — We shall first assume that the two solvents are not soluble in each other. We apply 129 directly to such solutions, letting c' refer to one system and c to the other, providing the molecular weight of the body does not change on passing from one solvent to the other. When it does, we use 131, and let c refer to that solvent in which the molecular weight of the solute is the greater.

PROBLEMS.

1. Let c_1 be the concentration of benzoic acid in grams per 1000 cc. of aqueous solution, c_2 that of the same substance in benzene per 1000 cc. solution.

$$c_1 = 1.50,\ 1.95,\ 2.89.$$

$$c_2 = 24.2,\ 41.2,\ 97.0.$$

What is the molecular weight of benzoic acid in water and in benzene? *Ans.* 122 in water, 244 in benzene.

K is strictly constant only when the molecules of solute are homogeneous in each solvent. Now in general this is not the case. In the above problem, practically *all* the benzoic acid molecules in water are normal, that is, there is only one set of molecules; but in benzene there are two sets, the normal and

the double, the latter, however, largely predominating. And the relative quantities of normal and double molecules change with the concentration. Hence we should not expect to find K constant unless we compare the same kind of molecule in the two solvents. When such corrections are made, K is much more constant.

2. How would you apply such a correction to the preceding problem?

3. In the following table, c_1 is the quantity in grams of ether in a unit volume of aqueous solution, c_2 the quantity in grams of ether in a unit volume of caoutchouc in contact with the aqueous solution. Temperature 20.5° to 22.5°.

$$c_1 = 1.24,\ 4.26,\ 5.66,\ 6.99,\ 7.93.$$

$$c_2 = 3.85,\ 16.14,\ 24.49,\ 31.43,\ 38.09.$$

Freezing-point determinations show that in water, ether is in the form of simple molecules only.

It is evident that neither c_1/c_2, nor c_1^2/c_2, nor any other ratio of c_1 and c_2 gives a constant value for K.

Plotting the values of c_1/c_2 for small values of c_1 and c_2 (not given in the table), in which case the molecules of ether in water and in caoutchouc are presumably both simple, we find the value 0.357. That is, the quantity of ether which dissolves in water, compared with the quantity of ether as *simple* molecules in caoutchouc, is 0.357. Now this ratio should be constant, and therefore we can calculate the quantity of ether in caoutchouc as simple molecules when the quantity in the aqueous solution in contact with the caoutchouc is known. The rest of the ether in the caoutchouc may be double molecules or triple ones, or perhaps still more complex. Making this correction, we get a much more constant value for K.

What is the corrected value for K? *Ans.* 3.958.

4. A composite crystallin mass of β naphthol in naphthalin as solid solvent is shaken up with H_2O until H_2O is saturated at

25° C. In the table, m_1 = mass of naphthalin, m_2 = mass of β naphthol in the crystals, M_1 = mass of β naphthol left in the solid solution after extraction, M_2 = mass of β naphthol in 100 cc. solution after extraction, all in grams; v = volume of β naphthol in V, V = volume in cc. of solid occupied by $m_1 + M_1$ after extraction.

m_1.	m_2.	M_1.	M_2.	v.	V.
7.999	2.004	1.937	0.0449	1.592	8.538
6.008	4.003	3.901	0.0680	3.205	8.422
4.004	6.002	5.885	0.0780	4.835	8.312
2.995	7.003	6.892	0.0743	5.663	8.264
1.998	8.001	7.890	0.0742	6.483	8.215
1.002	8.991	8.888	0.0742	7.303	8.173

At this dilution β naphthol in aqueous solution is of normal molecular weight. What is its molecular weight in the composite crystals? Why? *Ans.* 288.

5. What may we say about the molecular weight of the solid solvent, the naphthalin? Why? *Ans.* Mol. wt. = 256.

The student should notice that the quantity of the β naphthol dissolved by H_2O increases with the quantity of the β naphthol in the crystals up to a certain value, and then drops to a constant value. This would indicate that the β naphthol first added formed with the naphthalin a compound $C_{10}H_8O.C_{10}H_8$, that the β naphthol in this substance dissolved until free β naphthol appeared, and that then the solubility dropped to that of free β naphthol. See problem 3, page 123.

71. **Determination of molecular weights by depression in solubility of one liquid in another.** — We assume that liquid A is soluble in liquid B, but that B is not soluble in A. As solution corresponds to vaporization, whatever depresses the vapor pressure of A should likewise depress the solubility of A in B.

The relative depression in the vapor pressure of A is proportional to the number of grammolecules of a non-volatil solute in A. So the relative depression of solubility of A in B should be proportional to the number of grammolecules of a solute in A when the solute is insoluble in B.

Experiment supports this conclusion, for the results of such measurements agree with those obtained in other ways.

In the actual operation we have to use two liquids which are mutually soluble, the one in the other; but if B is not very soluble in A, and A is saturated with B before the measurements are made, there is but little interference on the part of B which dissolves in A; for a small quantity of one solute in a liquid does not interfere in the determination of the molecular weight of a second solute, provided there is no chemical reaction.

Let s_0 be the solubility of A in B, s_1 the solubility of A in B after addition of solute to A. The solubility is the mass in grams of A in the unit volume of solution. Then from 78, if α is a constant,

$$\frac{n}{N+n} = \alpha \frac{s_0 - s_1}{s_0}. \qquad 161$$

Since $n = w/m$ and $N = W/M$, where m, M, are the molecular weights of solute and solvent, and w, W, are their masses respectively,

$$m = \frac{w}{W} \cdot \frac{M}{\alpha} \cdot \frac{s_1}{s_0 - s_1}. \qquad 162$$

This equation presupposes that there is no appreciable change in volume after the solute has been dissolved. As a matter of fact, there is an appreciable change; but the correction is easily applied, for the relative solubility, when there is a change in volume, becomes

$$\frac{s_1}{s_0 - s_1} \cdot \frac{V_0}{V} \text{ instead of } \frac{s_1}{s_0 - s_1},$$

where V_0 is initial volume, V volume after solute has been dissolved; so

$$m = \frac{w}{W} \cdot \frac{M}{\alpha} \cdot \frac{V_0}{V} \cdot \frac{s_1}{s_0 - s_1}. \qquad 163$$

Problems.

1. Phenol is the solvent whose solubility is depressed by a solute. A saturated solution of NaCl is the liquid in which the phenol dissolves. So M and W refer to phenol. V_0 is constant, $W = 10$ grams. Chloroform is the solute.

w in grams.	V.	Quantity C_6H_5OH in NaCl solution in arbitrary units.
——	10	108.10
0.2793	10.18	105.55
1.7358	11.16	95.20
3.4879	12.32	86.20

What is the mean value of α? *Ans.* 0.892.

2. 0.1123, 1.0727, grams of a substance were dissolved in 10 grams phenol. $s_0 = 36.03$; $s_1 = 35.75$, 33.12, respectively. $V = 10.08$, 10.72 respectively. What is m? *Ans.* 119.

3. Equation 163 can give us a clue as to the correctness of the assumption following problem 5, page 121, if we consider β naphthol as the solvent whose solubility is depressed by dissolving naphthalin in it. Assuming that the composite crystals are $(C_{10}H_8)_n$ and $C_{10}H_8O$ only, we have, from the table on page 121, for substitution in 163, $s_1 = 0.0449$, 0.0680, 0.0780; $m = (128)_n$; $M = 144$; $W = 1.937$, 3.901, 5.885; $w = 7.999$, 6.008, 4.004; $V = 8.538$, 8.422, 8.312; $V_0 = 1.592$, 3.205, 4.835; $\alpha = 0.892$; $s_0 = ?$

We stop after the third value, for there the appearance of free β naphthol complicates matters.

Is s_0 constant? Does it agree with the observed solubility for different values of n? What does this show in regard to n?

4. Assuming now that the solvent is $xa C_{10}H_8 ya C_{10}H_8O$, such that x and y are the number of molecules of each body and $x + y = n$, and that $n = 2$, we have, for the mass of the solid solvent,

$$W = 1.937 + 1.937 \cdot 128/144,\ 3.901 + 3.901 \cdot 128/144,$$
$$5.885 + 5.885 \cdot 128/144;$$

$$w = 7.999 - 1.937 \cdot 128/144,\ 6.008 - 3.901 \cdot 128/144,$$
$$4.004 - 5.885 \cdot 128/144;$$

$$m = 256;$$

V_0 = volume of solvent; calculate it.

The other quantities are as in problem 3. $s_0 = ?$ Is it constant? Does it agree with the observed solubility? Would it be seriously changed by putting $n = 3$, 4, etc.? What does it show in regard to the assumption on page 123?

CHAPTER VI.

CHEMICAL KINETICS.

72. **Chemical kinetics.** — Sometimes called chemical dynamics. It treats of the velocity of chemical reactions.

In the previous chapter we considered the condition of the system after reaching equilibrium, now we shall consider the system from the time the components are mixed to the time when the system reaches equilibrium.

Let dx be the fraction of a grammolecule changed in time dt. We assume that dx is proportional to the concentration in grammolecules of unchanged substance or substances at the instant from which dt is measured. This is justified by agreement of theory and experiment. Let aA, bB, $cC, \cdots$ be the initial quantities in grammolecules which react, and choose x so that it is numerically the same for all the reacting bodies. This will be the case when a, A, b, B, c, C, etc., are expressed in equivalents. Then the hypothesis has the analytical form

$$\frac{dx}{dt} = kc_1c_2c_3\cdots = k\frac{a-x}{V}\cdot\frac{b-x}{V}\cdot\frac{c-x}{V}\cdots, \qquad 164$$

where A, B, $C, \cdots$ in equivalents react thus,

$$A + B + C + \cdots = P + Q + R + \cdots.$$

This k is not the same as K of the preceding chapter, but it is a constant as K is. In this form dx/dt seems to be independent of the products of the reaction, P, Q, $R, \cdots$. But as we have seen in the preceding chapter P, Q, $R, \cdots$ react to form A, B, $C, \cdots$ back again. Hence dx/dt should be looked upon

as the difference between the two velocities dx'/dt and dx''/dt; that is,

$$\frac{dx}{dt} = \frac{dx'}{dt} - \frac{dx''}{dt},$$

where dx' refers to

$$A + B + C + \cdots = P + Q + R + \cdots,$$

and dx'' to $\quad P + Q + R + \cdots = A + B + C + \cdots.$

73. **Monad reactions.** — Monad reactions are those in which only one body is to be considered as reacting.

For instance, when sugar decomposes under the influence of an acid into dextrose and levulose,

$$C_{12}H_{22}O_{11} + H_2O + HR = C_6\overset{+}{H}_{12}O_6 + C_6\overset{-}{H}_{12}O_6 + HR.$$

The acid is not represented as ionized, for our attention is to be given to the sugar and its products, and as the acid is found at the end of the reaction, just as it was at the beginning, we need not consider it as a reacting body. The water, on the other hand, is a reacting body; but as the reaction is, for the present, supposed to take place in dilute solution, the quantity of water is practically constant, and is therefore to be absorbed in the constant. With this understanding, the velocity equation for the decomposition of sugar becomes

$$\frac{dx}{dt} = k_1 \frac{a - x}{V} = k(a - x), \qquad 165$$

where a is the initial quantity of sugar in grammolecules, and V is the volume in liters. It is usual to keep V constant and absorbed in k.

Before this equation can be tested experimentally it must be integrated. Doing so, we get

$$\int \frac{dx}{a - x} = kdt \text{ or } -l(a - x) = kt + \text{constant}.$$

The constant can be eliminated by remembering that when $t = 0$, $x = 0$, and so

$$\text{constant} = -la.$$

Hence $$l\frac{a}{a-x} = kt \text{ or } \frac{1}{t}l\frac{a}{a-x} = k. \qquad 166$$

PROBLEMS.

1. $a = 0.453$ grammolecules sugar in 1000 cc. solution; $t = 0$. When $t = 1435$ mins., $x = 0.034$; $t = 11360$ mins., $x = 0.140$. What is the mean value of k? *Ans.* 0.0_4233.

2. Dibromsuccinic acid decomposes in aqueous solutions thus:

$$C_4H_4O_2Br_2 = HBr + C_4H_3O_2Br.$$

The decomposition is determined with 1/2 normal $Ba(OH)_2$ solution; n = number of cc. $Ba(OH)_2$ used to neutralize 10 cc. of dibromsuccinic acid solution. Time in minutes;

$t =$	0,	8,	10,	22,	30,	39,	60,	90.
$n =$	10.21,	11.25,	11.55,	12.84,	13.3,	13.71,	14.52,	15.03.

What is the mean value of k? *Ans.* 0.0_3189.

3. Show that at a time t the quantity remaining, $(a - x)$, is independent of the volume.

Monad reactions are so simple we shall not consider any more of them.

74. **Diad reactions.** — In this case 164 becomes

$$\frac{dx}{dt} = k_1\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right). \qquad 167$$

Keeping V constant and integrating,

$$\int\frac{dx}{(a-x)(b-x)} = \int kdt \text{ or } \frac{1}{a-b}l\frac{a-x}{b-x} = kt + \text{constant}.$$

When $t = 0$, $x = 0$, and so

$$\frac{1}{a-b} l \frac{a}{b} = \text{constant},$$

whence

$$\frac{1}{a-b} l \left(\frac{b}{a} \cdot \frac{a-x}{b-x} \right) = kt. \qquad 168$$

When $a = b$, equal numbers of grammolecules of the reacting bodies are present at the outset, and 168 becomes indeterminate.

But in this case, 167 becomes

$$\frac{dx}{dt} = k_1 \left(\frac{a-x}{v} \right)^2. \qquad 169$$

Integrating, assuming v is constant,

$$\frac{x}{(a-x)a} = kt. \qquad 170$$

Example. — Sodium chloracetate reacts with NaOH in aqueous solution thus;

$$CH_2ClCO_2Na + NaOH = CH_2OHCO_2Na + NaCl.$$

We start with $a = b = 1$. When $t = 0$, 10 cc. of solution need 14.9 cc. normal HCl for neutralization. Put the number of cc. HCl needed $= w$. When $t = 9$, $n = 14.10$. Hence 0.8 parts of a have disappeared $= x$. This gives $k = 0.0_3 42$. In a similar way we find from the following data the average value of k to be $0.0_3 40$.

$t =$	29,	89,	141,	254.
$n =$	12.75,	10.00,	8.00,	5.95.

Problems.

1. Maleic acid reacts thus in aqueous solution with Br;

$$C_2H_2(COOH)_2 + Br_2 = C_2H_2Br_2(COOH)_2.$$

Let $x =$ fraction of grammolecule of Br which has combined at time t.

$t = 0,$	90,	160,	280,	450.
$x = 0,$	0.25,	0.39,	0.49,	0.59.

What is the mean value of k? *Ans.* 0.00358.

2. For funearic acid under the same conditions and for the same time,

$x = 0,$	0.11,	0.17,	0.23,	0.29.

What is the mean value of k? *Ans.* 0.00115.

The student will have observed that the constancy of k is not satisfactory; possibly the measurements were not carefully made, or the acids were not pure. Notice the difference in the k for the two acids. How do you explain it?

3. Ethyl acetate, when treated with MOH, reacts thus;

$$CH_3CO_2C_2H_5 + MOH = CH_3CO_2M + C_2H_5OH.$$

When M is potassium and $t = 0$, the number of cc. of an acid required to neutralize 10 cc. of solution is 5.964. Call this n,

$t = 3.45,$	7.43,	21.98,	∞.
$n = 5.146,$	4.424,	3.077,	1.098.

What is the mean value of k? Notice KOH is in excess.

Ans. 0.0208.

4. When M = Ba,

$t = 0,$	3.63,	10.52,	29.89,	∞.
$n = 73.72,$	63.89,	52.52,	39.1,	27.69.

What is the mean value of k? *Ans.* 0.0182.

5. One grammolecule each of two reacting bodies are contained in 1000 cc. of solution in the first case, and in 4000 cc. in the second case. At the end of time t, how much more or less has changed in the second case than in the first case?

Ans. $x_2 = x_1 a/(4a - 3x_1)$.

75. **Triad reactions.** — Equation 164 becomes

$$\frac{dx}{dt} = \frac{k(a-x)}{v}\frac{(b-x)}{v}\frac{(c-x)}{v}. \qquad 171$$

Assuming v constant, and integrating,

$$\frac{1}{(b-a)(c-a)} \cdot l\frac{a}{a-x} + \frac{1}{(a-b)(c-b)} \cdot l\frac{b}{b-x}$$

$$+ \frac{1}{(a-c)(b-c)} \cdot l\frac{c}{c-x} = kt. \qquad 172$$

When $a = b = c$,

$$\frac{dx}{dt} = k\frac{(a-x)^3}{v^3}. \qquad 173$$

Assuming v constant, and integrating,

$$\frac{x(2a-x)}{2a^2(a-x)^2} = kt. \qquad 174$$

The triad reactions so far known do not give satisfactory constancy for k.

It is evident that here also x is dependent upon v.

76. **Number of molecules in a reaction.** — In the chapter on Equilibrium we saw how K could be made to show the form of the reaction; that is, the number of different molecules taking part. In a similar way this k may be used.

Example. — Arsine may decompose thus;

$$4\,AsH_3 = As_4 + 6\,H_2, \qquad 175$$

or thus;

$$AsH_3 = As + 3H. \qquad 176$$

In the first case,

$$\frac{3a^2x - 3ax^2 + x^3}{3a(a-x)^3 t} = k; \qquad 177$$

in the second,

$$\frac{1}{t} l\frac{a}{(a-x)} = k. \qquad 178$$

When $t = 0$, pressure is 785 mm. Hg;

$t =$	3,	5,	7,	8.
$p =$	878,	928,	969,	987.

The initial pressure may be supposed to be the pressure of 4 grammolecules of AsH_3, or of 1 grammolecule, according to whether we consider 177 or 178.

In the first case, an increment of pressure of 3 units means a decrease of 4 grammolecules of AsH_3, so

$$x = \frac{p - 785}{785} \cdot \frac{4}{3}.$$

In the second case, an increment of pressure of 1.25 units means a decrease of 1 grammolecule of AsH_3, so

$$x = \frac{p - 785}{785} \cdot \frac{1}{1.25}.$$

Substituting the first value for x in 177, and the second in 178, we find that in the second case k is much more constant than in the first one. So we are to consider 176 as more probably representing the decomposition of AsH_3.

Sometimes the reactions are of such a nature that accurate experimental observations are difficult or impossible, and the values for k are in no case constant. Then, by changing the initial concentrations very much, it will generally be found that in one case k is much more constant than in any of the other cases.

CHAPTER VII.

PHASES.

77. **Conditions of equilibrium.** — From 18, 11, and 46, we have

$$dU = TdS - pdv. \qquad 179$$

When the system is composed of several bodies whose masses are subject to changes, we must introduce into this equation terms referring to these quantities. If $w_1, w_2, \cdots w_n$ are the masses of n constituents each independently variable, and the total mass of the system is kept unchanged, 179 becomes

$$dU = TdS - pdv + \mu_1 dw_1 \cdots \mu_n dw_n, \qquad 180$$

where

$$\mu = \frac{\partial U}{\partial w}. \qquad 181$$

When the entropy of the system is unchanged, the condition of equilibrium is, by 103,

$$\partial U \geqq 0.$$

In a system composed of n independently variable constituents, the condition of equilibrium may be written

$$\partial U_1 + \partial U_2 + \cdots \partial U_n \geqq 0; \qquad 182$$

or if we consider the system divided into r parts or *phases*, as we shall call the parts, each phase containing the n constituents, we have the condition of equilibrium,

$$\partial U' + \partial U'' + \cdots \partial U^r \geqq 0. \qquad 183$$

Bodies which differ in state or composition are examples of different *phases* of matter; so a phase is to be defined as a state or composition of matter. Equation 182 may be written

$$T'\partial S' - p'\partial v' + \mu_1\partial w_1 + \cdots + \mu_n{}'\partial w_n{}' + T''\partial S'' - p''\partial v'' + \mu_1{}''\partial w_1{}''$$
$$+ \cdots \mu_n{}''\partial w_n{}'' + \cdots + T^r\partial S^r - p^r\partial v^r + \mu_1{}^r\partial w_1{}^r + \cdots + \mu_n{}^r\partial w_n{}^r \geqq 0. \quad 184$$

Since the changes are internal changes,

$$\partial S' + \partial S'' + \cdots + \partial S^r = 0, \quad 185$$
$$\partial v' + \partial v'' + \cdots + \partial v^r = 0, \quad 186$$
$$\partial w_1{}' + \partial w_1{}'' + \cdots + \partial w_1{}^r = 0, \quad 187$$
$$\cdots\cdots\cdots\cdots$$

and therefore to satisfy 182 we have to impose the conditions

$$T' = T'' = T''' = \cdots = T^r, \quad 188$$
$$p' = p'' = p''' = \cdots = p^r, \quad 189$$
$$\mu_1{}' = \mu_1{}'' = \mu_1{}''' = \cdots = \mu^r, \quad 190$$
$$\cdots\cdots\cdots\cdots$$
$$\mu_n{}' = \mu_n{}'' = \mu_n{}''' = \cdots = \mu_n{}^r. \quad 191$$

That is, the *temperature and pressure of each phase must be the same throughout the system.* The terms $\mu \cdots$ are called the *potentials* of the phases. So *at equilibrium, the potentials of the different phases have the same value.*

When the values of the variables S, v, w, in 184 are known, the state of the system is completely described. The number of these variables which are independent are $(n+2)r$, where r is the number of phases in the system.

The quantities in 188–191 are functions of these variables, so that when the energy of each phase is given in terms of entropy, volume, and mass of the components, T, p, μ, are determined. The number of these equations is $(n+2)(r-1)$.

They are independent equations between the independent variables.

The volume of the whole system and the total mass of its components are known, which give $n + 1$ additional equations, so that when we know the total energy or the total entropy of the system, we have

$$(n + 2)(r - 1) + n + 1 + 1 = (n + 2)r$$

equations between the $(n + 2)r$ independent variables.

Each of the r phases may not contain the n components. Then ∂w, which refers to the bodies which are not components of all the phases, cannot become negative in 184. Therefore for equilibrium in the system it is not necessary that the potentials referring to these substances should have the same value in every phase of the system; it is only necessary that those potentials should have the same value in every phase which refer to the actual components of the phases in question. For the other phases which have not the same components, it is only necessary that the potentials of the possible component bodies in these phases should not have a smaller value than they have in the phases in which the bodies are actual components.

Integrating 180 between 0 and some finite value,

$$U = TS - pv + \mu_1 w_1 + \mu_2 w_2 + \cdots + \mu_n w_n. \qquad 192$$

Differentiating in the most general way,

$$dU = SdT + TdS - pdv - vdp + \mu_1 dw_1 + w_1 d\mu_1 + \cdots + \mu_n dw_n + w_n d\mu_n; \qquad 193$$

and comparing with 179,

$$vdp = SdT + w_1 d\mu_1 + \cdots + w_n d\mu_n. \qquad 194$$

78. **Coexistent phases.** — Coexistent phases are phases which can exist together.

When a system of one phase is composed of n independently variable compounds, we can make $n + 1$ independent changes.

When there are r coexistent phases, each containing n independently variable components, the system is capable of $n+1-(r-1)$ independent changes, and still remain in equilibrium. For equations 188 to 191 show that temperature, pressure, and potentials must be constant for each of the n components taken separately, and 194 applied to each phase shows that these quantities are subject to as many conditions as there are different phases.

When the r phases have not the same n components, though the system as a whole contains n independently variable components, there are the same $n+2-r$ independent changes.

79. **Monad systems.** — Systems containing one component are called monad systems.

Example. — Water. In this case 184 becomes

$$T\partial S - p\partial v + \mu\partial w = 0.$$

As this one phase is given, w is fixed, and we have the two independent variables S and v. It is more convenient, however, to use T and p instead of S and v. We may do this, for we have seen that these quantities are connected with each other. How are they connected?

So when $r=1$, we may change T and p independently within wide limits without losing the phase. At certain values for T and p, the given phase disappears, to be replaced by another. When the given phase has completely disappeared, p and T may again be changed independently within wide limits until the second phase disappears, to be replaced by a third one perhaps.

Starting with vapor at a certain pressure and temperature, and increasing p while T is constant, we get the liquid phase. Diminishing T and keeping p constant, we pass into the solid phase. Starting with ice at a certain pressure and temperature, and increasing p while T is kept constant, we get either the gas or liquid phase, depending upon the initial p.

When $r=0$, that is, when we consider water without speci-

fying any particular phase, we have three independent indefinite quantities, S, v, w, or T, p, μ, and no equation to connect them, and the system has three independent changes.

When $r = 1$, we have the same variables but the equation for the one phase,

$$T\partial S - pdv + \mu\partial w = 0,$$

to connect them, so that the system has only two independent changes.

When $r = 2$, we have the same variables but the two equations for the two phases,

$$\begin{aligned} T'\partial S' - p'\partial v' + \mu'\partial w' &= 0, \\ T''\partial S'' - p''\partial v'' + \mu''\partial w'' &= 0, \end{aligned}$$

to connect them, so that the system has only one independent change.

Suppose the initial system consists of ice and water. The one independent variable may be either temperature or pressure, but not both independent at once. When we change p arbitrarily, without allowing T to change correspondingly, one of the phases disappears, leaving but one phase, water or ice. Similarly with ice and vapor, or liquid and vapor. But when we adjust the two quantities p and T properly, then we can change them without losing either phase.

When $r = 3$, we have the three equations, one for each phase,

$$\begin{aligned} T'\partial S' - p'\partial v' + \mu'\partial w' &= 0, \\ T''\partial S'' - p''\partial v'' + \mu''\partial w'' &= 0, \\ T'''\partial S''' - p'''\partial v''' + \mu'''\partial w''' &= 0, \end{aligned}$$

and an independent change of either variable is impossible.

It does not seem possible that r can ever be greater than the number of independent variables. This is a conclusion from experience only.

These statements will appear clearer from a study of the

accompanying figure. Let the abscissa of Fig. 10 represent the temperatures, and the ordinates, the pressures. These two variables are more convenient than T, μ, or p, μ. Let us start with water vapor at some temperature and pressure corresponding to a where p is not too low. Diminish T, keeping p constant. The locus will be ab. At b, a second phase, the liquid phase appears, and we cannot *diminish* T at that particular p any further without losing the initial phase, the vapor

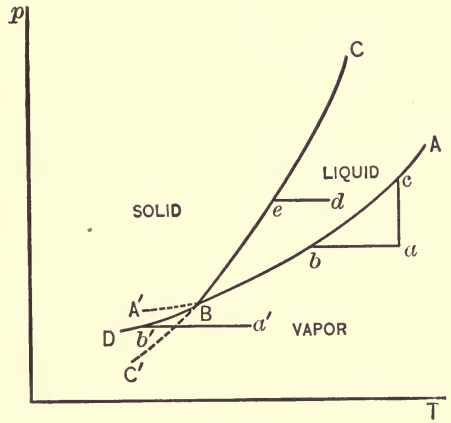

FIG. 10.

phase. But we may *increase* T at that particular p up to the total decomposition of the vapor without losing it. Of course, as the decomposition proceeds, the vapor disappears; but that is an entirely different sort of action, not to be included in the present considerations. So b marks the lower limit of T at which water vapor can exist at the particular p.

Starting from the same point a and keeping T constant, let us increase p. The locus will be the line ac. At c the liquid phase again appears, and at that particular temperature p cannot be increased without losing the vapor phase. We may diminish p at that particular temperature indefinitely without

losing the vapor phase. So if we move a about and mark the values of p and T at which liquid appears, we shall get a curve AB, which gives the values of p and T at which liquid and vapor coexist. For any value of T to the right of this curve, and of p below it, only the vapor phase exists.

We might expect that for any value of T to the left of this curve, and for any value of p above it, only liquid phase existed. This is partly true; it is true until a solid phase appears. If we start from a point d in the liquid phase and diminish T while p is constant, we shall reach a value for T at which the solid phase appears. Just as we get the curve AB, the curve of coexistent liquid and vapor, so we can get the curve CB, the curve of coexistent liquid and solid. For every value of p and T between AB and CB only liquid exists. For every value of p and T to the left of CB and above it, only solid exists.

Had we started at a' instead of at a, where p is very low, and diminished T while p was kept constant, the solid phase would have appeared instead of the liquid phase, and we should have obtained the curve BD, which is the curve of coexistent vapor and solid.

At B the three phases are coexistent. As B is a point of intersection of three curves, there is no variation possible; it is fixed. So the three phases can only coexist at a certain *fixed* p and T.

In some cases, by very careful management, it is possible to cool a liquid below its freezing point or heat it above its boiling point; to heat a solid above its melting point or vaporization point; to cool a vapor below its liquefaction point or solidification point. Then the curves will not stop at B, but continue some distance beyond B, as shown by the dotted lines. As these are cases of unstable equilibrium, and have not been well worked out, we pass them by.

80. **Diad systems.** — A diad system is a system composed of two different components, such as a solvent and a solute. Not

very many such systems have been worked out. A good example is sulfur dioxid and water.

Four phases are possible when $r = 0$ for $n + 2 - r = 4$, since $n = 2$. What the phases may be, is largely to be determined by experiment. There may be any number of phases taken separately; the rule $n + 2 - r =$ number of phases, is only true for coexistent phases.

More than one gaseous phase is by the nature of the case excluded.

When $r = 1$, the equation of equilibrium becomes

$$T\partial S - p\partial v + \mu_1 \partial w_1 + \mu_2 \partial w_2 = 0.$$

As there is only one equation between the four variables, there are three independent variables, and the system cannot well be represented in a space of two dimensions.

When $r = 2$, the equations of equilibrium are

$$\begin{aligned} T'\partial S' - p'\partial v' + \mu_1'\partial w_1' + \mu_2'\partial w_2' &= 0, \\ T''\partial S'' - p''\partial v'' + \mu_1''\partial w_1'' + \mu_2''\partial w_2'' &= 0, \end{aligned}$$

one for each phase. In this case there are only two independent variables, and so we can represent such a system by the indefinite area in the pT plane of Fig. 11.

When $v = 3$, the equations of equilibrium are

$$\begin{aligned} T'\partial s' - p'\partial v' + \mu_1'\partial w_1' + \mu_2'\partial w_2' &= 0, \\ T''\partial s'' - p''\partial v'' + \mu_1''\partial w_1'' + \mu_2''\partial w_2'' &= 0, \\ T'''\partial s''' - p'''\partial v''' + \mu_1'''\partial w_1''' + \mu_2'''\partial w_2''' &= 0. \end{aligned}$$

In this case, there is only one independent variable, and so we get a line in the pT plane showing the necessary relations between p and T for the existence of three phases.

At A of Fig. 11, four phases coexist. They are the gaseous phase, $SO_2 + zH_2O$; a solution of SO_2 in H_2O, $H_2O + xSO_2$; a solution of H_2O in SO_2, $SO_2 + yH_2O$; the solid phase, $SO_2 . 7\,H_2O$.

When a particular series of relations between p and T is maintained, the solution of H_2O in SO_2 disappears, and we get

the curve AB, which shows the relation between these variables necessary for the coexistence of vapor, solution of SO_2 in H_2O and solid $SO_2 . 7\,H_2O$.

At B a fourth phase appears, unless we proceed very carefully in the cooling. In such a case it is possible to prevent the new phase from appearing, and the curve continues along the dotted line. But the system is now in a state of unstable equilibrium, and we shall not consider this curve. The new

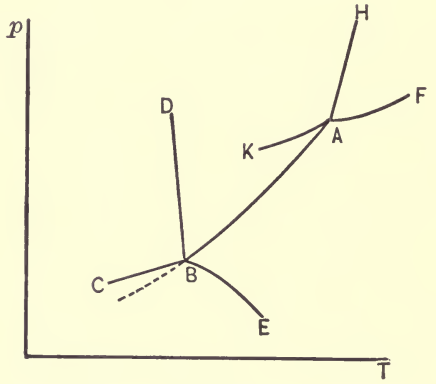

FIG. 11.

phase is frozen H_2O. Having four phases coexisting, no further change of p or T is possible without losing one of the phases.

If the conditions are such that a decrease of T does not decrease p much, then the solution of SO_2 in H_2O disappears, and we get the curve BC, which shows the relation between p and T necessary for the coexistence of ice, solid $SO_2 . 7\,H_2O$, and vapor $SO_2 + zH_2O$.

On the other hand, if p rises very much when T decreases, the vapor phase disappears, and we get the curve BD which shows the relation between p and T necessary for the coexistence of ice, solid $SO_2 . 7\,H_2O$, and solution of SO_2 in H_2O.

Finally, if we increase T, at the same time arranging matters

so that p can be diminished, we lose the solid phase and get the curve BE, different from AB. This curve gives the relation between p and T necessary for the coexistence of ice, solution of SO_2 in H_2O, and the vapor phase $SO_2 + zH_2O$.

Returning to A and increasing T and p, the latter not very much, the solid phase $SO_2 . 7\ H_2O$ disappears, giving the curve AF, which shows the relation between p and T necessary for the coexistence of the vapor phase and the two liquid phases, $SO_2 + yH_2O$, $H_2O + xSO_2$.

On the other hand, if p increases greatly as T increases, the vapor phase disappears, and we get the curve AH, which shows the relation between p and T necessary for the coexistence of the solid phase and the two liquid phases.

Finally when p diminishes less rapidly than in the case in which AB is developed, the solution of SO_2 in H_2O disappears, and we get the curve AK, which shows the relation between p and T necessary for the coexistence of the vapor, $SO_2 + yH_2O$, and solid $SO_2 . 7\ H_2O$.

The compositions of the different phases, the values for x, y, z, have been carefully determined. We need not consider them.

A similar set of curves have been obtained for ferric chlorid and water.

The four coexistent phases are H_2O vapor, solution of $FeCl_3$ in H_2O, and two hydrates, $FeCl_3 . mH_2O$ and $FeCl_3 . nH_2O$. The values for m and n are 0, 4, 5, 7, 12, ∞. The last value corresponds to solid H_2O. Probably at a high temperature the vapor phase contains $FeCl_3$.

With HBr and H_2O, a very instructive set of curves is obtained.

The curve ACB, Fig. 12, shows the necessary relation between p and T for equilibrium between the three phases $HBr . 2\ H_2O$ solid, $H_2O + xHBr$ liquid, and $HBr + zH_2O$ vapor. As we proceed from A to C, that is as p and T increase, HBr in the liquid phase also increases, as we may expect it to do.

At C, $x = \frac{1}{2}$, so that the solid and liquid phases have the same composition. At this point the hydrate melts. If now we diminish T but increase p, HBr in the liquid phase increases and the solid $HBr.2H_2O$ reappears, giving the curve CB.

Since at C liquid and solid have the same composition, we may look upon the liquid phase, at this particular point, as melted solid and C as the melting point at p pressure. On

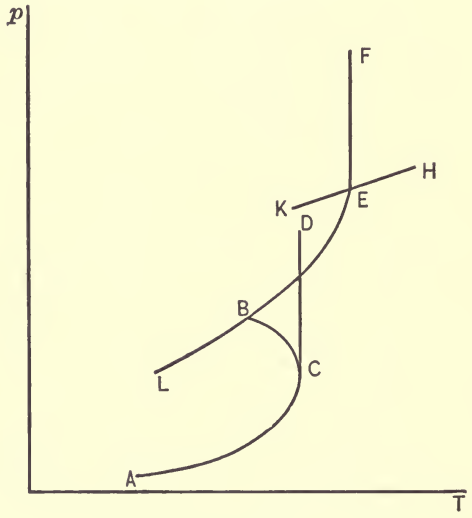

FIG. 12.

increasing p very much, in which case the vapor phase must disappear, while diminishing T, we get the curve CD, which shows the relation between p and T necessary for the coexistence of the solid phase $HBr.2H_2O$ and the liquid phase $HBr.2H_2O$. So in this particular part of the consideration, $n = 1$, $r = 2$, and there is but one independent variable.

At B the solid phase $HBr.2H_2O$ loses one H_2O, changing into $HBr.H_2O$. At this point, therefore, the four coexistent

phases are $HBr.2H_2O$ solid, $HBr.H_2O$ solid, $H_2O + xHBr$ liquid, $HBr + zH_2O$ vapor.

PROBLEM.

Have we four coexistent phases at c? Why?

The curve BE gives the relation between p and T necessary for the coexistence of $HBr.H_2O$ solid, $H_2O + xHBr$ liquid, and $HBr + zH_2O$ vapor. So to a certain extent BE corresponds to AC, but not entirely, for before the liquid phase contains as much HBr as the solid phase, another liquid phase, $HBr + yH_2O$, appears; y is very small. The HBr in $H_2O + xHBr$ increases from B to E. At B, $x = 0.61$; at E, $x = 0.83$.

At E we have the four coexistent phases, solid $HBr.H_2O$, liquid $H_2O + 0.83$ HBr, liquid $HBr + yH_2O$, and vapor $HBr + zH_2O$.

If now we raise p very much and increase T, in which case the vapor phase must disappear, we get the curve EF, which shows the relation between p and T necessary for the coexistence of solid $HBr.H_2O$, liquid $H_2O + xHBr$, liquid $HBr + yH_2O$.

On the other hand, if we diminish p and T in the proper way, we get the curve EK, which shows the relation between p and T necessary for the coexistence of the three phases, solid $HBr.H_2O$, liquid $HBr + yH_2O$, and vapor $HBr + zH_2O$.

If we increase p and T in the proper way, we get the curve EH, which shows the relation between p and T necessary for the coexistence of the three phases, liquid $HBr + xH_2O$, liquid $HBr + yH_2O$, vapor $HBr + zH_2O$.

Returning to B, if we diminish p and T, the liquid phase $H_2O + xHBr$ may disappear and give us the curve BL, which shows the relation between p and T necessary for the coexistence of the three phases, solid $HBr.2H_2O$, solid $HBr.H_2O$, vapor $HBr + zH_2O$.

81. **Thermodynamic relations.** — Let Q be the heat required

to change, at constant p and T, one grammolecule of the system from one state to another state. Then, we have from 42,

$$dW = \Delta v dp = Q\frac{dT}{T},$$

or

$$T\frac{dp}{dT} = \frac{Q}{\Delta v}, \qquad 195$$

where Δv is the change in volume of a grammolecule corresponding to the change in state considered. For the present we shall suppose that Q and Δv refer to a grammolecule of the *solid*. Assume that the vapor phase contains only one constituent. This is for simplicity. As H_2O is the far less volatile constituent, let us suppose it absent from the vapor phase. Let the solid phase contain a molecules of the gaseous constituent to one molecule of the other constituent. Let the liquid phase contain x molecules of the gaseous constituent to one molecule of the other constituent. In the HBr, H_2O system in general $a > x$. When one grammolecule of the solid phase disappears it produces one grammolecule of the liquid phase, and $a - x$ grammolecules of the vapor phase.

Let Q'' be the heat of fusion of one grammolecule of the solid phase.

Let Q' be the heat needed to expel the gaseous constituent from one grammolecule of the liquid when the concentration of the liquid passes from the concentration of a molecules gaseous constituent with one molecule other constituent to the concentration of x molecules gaseous constituent to one molecule other constituent. In other words, Q' is to represent the heat needed to change one grammolecule of the liquid from melted solid to the liquid phase proper.

Let v', v'', v''' be the molecular volumes of vapor, liquid, and solid. Then, 195 becomes

$$T\frac{dp}{dT} = \frac{Q'' + Q'}{v'(a - x) + v'' - v'''}. \qquad 196$$

Since $v'' - v'''$ is very small, this may be written

$$\frac{dp}{dT} = p\frac{Q'' + Q'}{RT^2(a-x)}. \qquad 197$$

When p and T are such that $a > x$, dp/dt is $+$; when $a = x$, $dp/dT = \infty$, for Q'' and Q' are both positive. When, however, $a < x$, then as the solid phase passes into the liquid, the gaseous constituent is absorbed from the vapor phase, and Q' passes out from the system, and therefore is $-$. In this case 197 becomes

$$\frac{dp}{dT} = p\frac{Q'' - Q'}{RT^2(a-x)}. \qquad 198$$

Hence as $a < x$, when $Q' < Q''$, dp/dT is $-$; when $Q'' = Q'$, $dp/dT = 0$; when $Q' > Q''$, dp/dT is $+$.

Let Q''' be the heat absorbed when one grammolecule of solid of molecular concentration a, in regard to the volatile constituent, dissolves in a liquid of molecular concentration x, in regard to the volatile constituent, the quantity of liquid being so great that its composition is not affected by the solution of the solid.

Then $$\frac{dW}{dT} = \Delta v\frac{dp}{dT} = \Delta v\frac{\partial p}{\partial x}\cdot\frac{\partial x}{\partial T} = \frac{Q'''}{T},$$

or $$\frac{\partial x}{\partial T} = \frac{Q'''}{\Delta v T}\cdot\frac{\partial x}{\partial p} = \frac{pQ'''}{RT^2(a-x)}\cdot\frac{\partial x}{\partial p}. \qquad 199$$

In the systems just considered, $SO_2 + H_2O$ and $HBr + H_2O$, Q''' and $\partial x/\partial p$ are positive, so that the sign of $\partial x/\partial T$ depends upon $a - x$. Collecting, we have the following cases:

$a > x$, $Q''' > Q'$, $\frac{dp}{dT}$ is $+$; Q''' is $+$, $\frac{\partial x}{\partial T}$ is $+$,

$a < x$, $Q'' > Q'$, $\frac{dp}{dT}$ is $-$; Q''' is $+$, $\frac{\partial x}{\partial T}$ is $-$,

$a < x$, $Q'' < Q'$, $\frac{dp}{dT}$ is $+$; Q''' is $+$, $\frac{\partial x}{\partial T}$ is $-$.

These cases correspond to three different parts of the equilibrium curve of a three-phase diad system. The divisions are to be made at those points where the curve runs either vertically or horizontally; that is, at those values of p and T for which

$$a = x, \quad Q' = 0, \quad \frac{dp}{dT} = \infty; \quad Q''' = Q' \text{ is } +, \quad \frac{\partial x}{\partial T} = \infty;$$

$$a < x, \quad Q'' = Q', \quad \frac{dp}{dT} = 0; \quad Q''' \text{ is } +, \quad \frac{\partial x}{\partial T} = -.$$

The general form of the equilibrium curve for three coexistent phases is given in Fig. 13. Starting from A, where dp/dT is

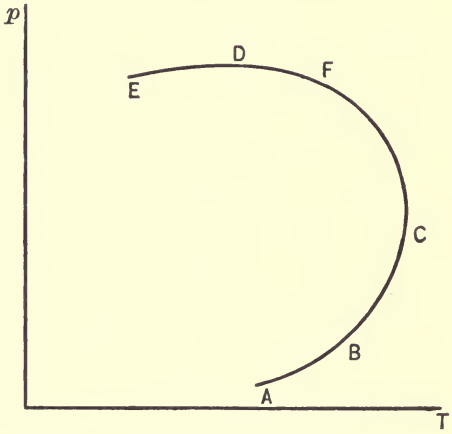

FIG. 13.

positive, the curve runs like AB. As p increases, x increases until $x = a$, and then $dp/dT = \infty$. This corresponds to the point C. After passing C as p still rises, $x > a$ and dp/dT becomes negative, giving the part CD. At D, $Q'' = Q'$, and so $dp/dT = 0$. From D to E, $Q'' < Q'$, but $x > a$, so dp/dT again becomes positive.

Compare this curve with the $HBr + H_2O$ curve. We see

that *ACB* in Fig. 12 corresponds to *ACF* in Fig. 13. But further than *F* it cannot be followed experimentally with the HBr system, for at *F*, or *B* of Fig. 12, the solid $HBr.2H_2O$ changes into the solid $HBr.H_2O$, and we pass to a curve belonging to a radically different system. In this second system we have the same number of phases and state, only the composition of the solid phase has radically changed. Hence the curve of equilibrium in this second system should correspond to that of Fig. 13. We see that it does, though limited to the part *AB* of this figure, for before *C* is reached, one of its phases disappears.

The curve *BE* of Fig. 12 corresponds to *AC* of Fig. 13, and not to *DE* of the same figure. For in *BE* of Fig. 12, $\partial x/\partial T$ is positive, whereas in Fig. 13, $\partial x/\partial T$ is only positive for *AC*, but not positive for *DE*, there it is negative.

Problem.

BE of Fig. 11 corresponds to what part of curve of Fig. 13?

Ans. CD.

CHAPTER VIII.

WHEN TEMPERATURE IS VARIABLE.

82. **The general equation for variable temperature.** — Differentiating 107, according to T, we get, with 108,

$$dW = RdTlK + RTd(lK).$$

Substituting in 42, we get with 107 and 108,

$$Q - W = Q_1 = RT^2\frac{d(lK)}{dT}. \qquad 200$$

Here Q is the total heat energy involved in the form of heat. Subtracting the heat energy used in internal work, we get Q_1 as the *heat of that particular reaction to which K belongs.* In the future we drop the suffix and write

$$\frac{d}{dT}lK = \frac{Q}{RT^2}. \qquad 201$$

This equation gives the change in the equilibrium constant with the temperature, provided no external work is performed during the change in temperature.

Integrating between T_1 and T_2,

$$lK_2 - lK_1 = l\frac{K_2}{K_1} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \qquad 202$$

We have assumed that Q is independent of T. Within narrow limits of T, this is undoubtedly admissible; but when T_1 and T_2 are wide apart it is not admissible, and we must know how Q depends upon T before we can accurately integrate 201.

In many cases the best we can do is to take the mean value for Q between T_1 and T_2.

83. **Decompositions producing vapors.** — For the general case in which gaseous bodies are produced from liquids and solids, as the liquids and solids have a constant concentration,

$$K = c_1^{n_1} c_2^{n_2} \cdots, \qquad 203$$

where c_1, c_2 $\cdots$ are the concentrations of the vapors and n_1, n_2 $\cdots$ the number of molecules of each substance involved in the change.

We may put

$$c = \frac{p}{T},$$

and then

$$K = \frac{p_1^{n_1} p_2^{n_2} \cdots}{T^{n_1+n_2+\cdots}}. \qquad 204$$

When the total pressure, P, is given,

$$p_1 = \frac{n_1}{n_1 + n_2 + \cdots} P.$$

PROBLEMS.

1. For water, when $t = 0°$, $p_1 = 4.5$ mm. Hg; when $t = 11.5°$, $p_2 = 10.0$ mm. Hg. What is Q? The logarithm of 202 is the natural logarithm. The modulus of the common system is 0.4343. *Ans.* 12040 cals.

2. Ammonium sulfhydrate decomposes on heating,

$$NH_4SH = NH_3 + H_2S.$$

The reaction is reversible. NH_4SH is solid. When $t = 9.5°$, $p_1 = 9.5$ cm. Hg; $t_2 = 25.1°$, $p_2 = 50.1$ cm. Hg. What is Q? *Ans.* 21600 cals.

84. **Solution.** — Solution corresponds to vaporization,

so

$$K = c,$$

where c is the concentration of the saturated solution, and therefore

$$l\frac{c_2}{c_1}=\frac{Q}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right). \qquad 205$$

The solubility of a solid at its fusion temperature, and the solubility of the fused solid at its fusion temperature, are the same in the same solvent.

PROBLEM.

Demonstrate why.

Let c_1 be the solubility of a body at T_1, the fusion temperature; let c_2'' be the solubility of the melted solid at T_2 and c_2''', the solubility of the solid at T_2; let Q''' be the heat of solution of the solid and Q'' that of the fused solid. We consider Q''' and Q'' independent of T. We have from 205

$$l\frac{c_2'''}{c_1}=\frac{Q'''}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right),$$

and

$$l\frac{c_2''}{c_1}=\frac{Q''}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right).$$

Subtracting,

$$l\frac{c_2'}{c_2'''}=\frac{Q''-Q'''}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right). \qquad 206$$

When a solid dissolves with evolution of heat, that is, when Q''' is negative, the numerical value of Q'' is always $Q''>Q'''$. Hence, considering the numerical relation,

$$Q''-Q'''>0.$$

Then when $T_2>T_1$, that is, when we compare solubility of solid and fused solid above the fusion temperature, we should find $c_2''>c_2'''$; that is, the liquid should be more soluble than the solid. On the other hand, below the fusion temperature, $T_2<T_1$, and then $c_2'<c_2'''$; that is, the liquid should be less soluble than the solid. The body, of course, is supposed to be in a superheated or under-cooled condition.

When the body absorbs heat on solution, the matter is more complicated, for then $Q'' - Q'''$ may be positive, negative, or equal to zero. Consider

$$Q'' - Q''' < 0.$$

Then at temperatures above fusion temperatures we should find $c_2'' < c_2'''$; that is, the solubility of the solid is greater than that of the liquid. At temperatures below fusion temperatures, $c_2'' > c_2'''$; that is, the solubility of the solid is less than that of the liquid.

When $$Q'' - Q''' = 0,$$

the solubility of solid and liquid should be equal.

PROBLEM.

For succinic acid in water, $t_1 = 0°$, $c_1 = 2.88\%$; $t_2 = 8.5°$, $c_2 = 4.22\%$. Supposing that the acid does not decompose in solution, what is Q? *Ans.* 6910 cals.

When the substance decomposes in solution into two other molecules, as

$$MR = M + R,$$

we have $$K = (c)^2,$$

and $$l\frac{K_2}{K_1} = \frac{Q}{2R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

PROBLEM.

For silver chlorid, $t_1 = 20°$, $c_1 = 1.10 \cdot 10^{-5}$; $t° = 30°$, $c_2 = 1.73 \cdot 10^{-5}$. What is Q, supposing the salt to be completely decomposed, and c to refer to grammolecules per liter? *Ans.* 16082 cals.

We see how the heat of solution can be determined for such slightly soluble bodies as silver chlorid. The concentration of the solution was determined electrolytically.

When the solute is a gas,

$$K = \frac{c'}{c} = \alpha,$$

so that for gases

$$l\frac{K_2}{K_1} = l\frac{\alpha_2}{\alpha_1} = -l\frac{\alpha_1}{\alpha_2} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

PROBLEM.

Assuming for CO_2 that $\alpha = 1.506 - 0.0365t + 0.000292t^2$, what is Q? *Ans.* 3902 cals.

85. **Decomposition of a gas.** — In this case

$$K = \frac{(c_1')^{n_1'}(c_2')^{n_2'} \ldots}{(c_1)^{n_1}(c_2)^{n_2} \ldots}.$$

Instead of substituting directly in 202, it is simpler to write the value of K for each special case.

EXAMPLE. — $2\,CO_2 = 2\,CO + O_2$.

So

$$K = \frac{(c_1')^2(c_2')}{(c)^2},$$

or in total pressure,

$$c_1' = p_1' = \frac{2x}{x+2}P;\quad c_2' = p_2' = \frac{x}{x+2}P;\quad c = \frac{2-2x}{x+2}P;$$

and

$$K = \frac{x^3}{(x+2)(1-x)}P.$$

Substituting in 202,

$$l\frac{K_2}{K_1} = l\left\{\frac{x_2^3(x_1+2)(1-x_1)}{x_1^3(x_2+2)(1-x_2)}\cdot\frac{P_2}{P_1}\right\} = \frac{Q}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}.$$

Q has been determined at different temperatures. Its value at any temperature T is

$$Q = Q_0 + c(T - T_0),$$

where Q_0 is the heat of the reaction at T_0, and c the specific heat of CO_2. Substituting Q, we can find x. In this way x, given for CO_2 on page 117, was determined.

86. **Change of velocity with the temperature.** — We see from 111 that the constant of equilibrium may be considered as a relation between two velocities and decomposable into two quantities, each referring to a single velocity. So 201 may be written

$$\frac{d(lK)}{dT} - \frac{d(lK')}{dT} = \frac{Q}{RT^2},$$

where, as before, Q is the heat of the reaction. Since the constant of velocity when decomposed has a similar significance to the constant of equilibrium, we may write in 201 the K of velocity as defined by 164, decomposing it also, so that

$$\frac{d(lk)}{dT} - \frac{d(lk')}{dT} = \frac{Q}{RT^2}.$$

Until k and k' are known the equation cannot be used in this form, but it can be written as

$$\frac{d(lk)}{dT} = \frac{A}{T^2} + B, \qquad 207$$

and B determined by experiment. B often reduces to zero, and then the velocity equation becomes identical with the equilibrium equation.

CHAPTER IX.

ELECTROCHEMISTRY.

87. **Units.** — There are three systems of electrical units.

(1) The absolute system expressed in c.g.s. units, measured electrostatically.

a. The unit quantity of electricity is the quantity of electricity which reacts with another equal quantity of electricity at a distance of 1 cm. across air with a force of 1 dyne.

b. A unit potential difference is the potential difference between two points when 1 erg of work is involved in moving unit quantity of electricity from one point to the other against electric force.

c. The unit density of electricity is the density of a unit quantity of electricity, when distributed uniformly over 1 cm^2.

d. The capacity of a body for electricity denotes the quantity of electricity needed to give it unit potential difference. In this system, a conducting sphere of 1 cm. radius has unit capacity.

e. The quantity of electricity needed to produce a certain potential difference between two bodies separated by a substance A divided by the quantity of electricity required to produce the same potential difference between the same bodies in the same positions when separated by air, is called the specific inductive capacity or dielectric constant of A.

(2) The absolute system, or c.g.s. system, in electromagnetic units.

a. A unit magnetic pole is a pole that acts on an equal pole in air at a distance of 1 cm. with a force of 1 dyne.

b. A unit current of electricity is a current which in a wire of unit length, bent into the arc of a circle of unit radius, acts upon a unit pole at the center of the circle with a force of 1 dyne.

c. A unit quantity of electricity is the quantity conveyed by a unit current in one second.

d. Unit potential difference is the potential difference that must be maintained between the ends of a conductor in order that unit current shall do 1 erg in a second.

e. Unit conductivity is the conductivity that will allow unit quantity of electricity to pass in one second when the potential difference at the extremities of the conductor is unity. The reciprocal of the conductivity is the resistance.

f. Unit capacity is the capacity of a condenser which is at unit potential difference when charged with unit electricity.

(3) The common system.

a. The unit quantity of electricity is the coulomb.

b. The unit of potential difference, commonly called electromotive force, is the volt. We shall denote potential difference by p.d.; volt, by V.

c. The unit of resistance is the ohm; the unit of conductivity is the reciprocal of the ohm, the mho.

d. The unit of current is one coulomb per second; it is called the ampere; the ampere is an intensity.

e. The unit of capacity is the farad.

The microfarad is the millionth of a farad.

The three systems are connected numerically thus:

One unit of p.d. in the electrostatic system is $= 3 \cdot 10^{10}$ units of p.d. in the electromagnetic system.

One coulomb $= 10^{-1}$ electromagnetic units in c.g.s. There is no quantity in the c.g.s. system that corresponds to the coulomb. But since 1 coulomb $\times$ 1 volt $= 10^7$ ergs, and 1 volt $= 10^8$ dynes, it follows that numerically 1 coulomb $= 10^{-1}$ electromagnetic units in c.g.s. Similarly for ohm, mho, ampere, farad.

One volt	$= 10^{8}$	dynes.
One ohm	$= 10^{9}$	electromagnetic units in c.g.s.
One mho	$= 10^{-9}$	electromagnetic units in c.g.s.
One ampere	$= 10^{-1}$	electromagnetic units in c.g.s.
One farad	$= 10^{-9}$	electromagnetic units in c.g.s.
One microfarad	$= 10^{-15}$	electromagnetic units in c.g.s.

The common system and the electromagnetic system are the systems in general use.

An ohm resistance is the resistance of a column of mercury 106.3 cm. long and 1 mm.^{2} cross section at 0°. Such a column has a conductivity of 1 mho.

The conductivity of any body is inversely as its length and directly as its cross section. That is,

$$c = \frac{a}{l},$$

where a is the cross section, l the length, and c the conductivity.

A Siemens unit of resistance, also called a mercury unit of resistance, is the resistance of a column of mercury 100 cm. long and 1 mm.^{2} cross section at 0°. This unit is generally used in measuring the conductivity of solutions.

There are also other units of resistance, so that caution in this respect is always needed when comparing data on conductivity from different sources.

A coulomb is also defined as the quantity of electricity needed to set free 0.0$_4$1036 grams of hydrogen.

88. **Ohm's law, Faraday's law, Joule's law.** — These laws are the foundations of all electrochemical considerations.

Ohm's law states that *the intensity of a current is equal to the potential difference into the conductivity* for the part of the circuit where the intensity is to be considered; or, *the intensity of a current is equal to the potential difference divided by the*

resistance for the part of the circuit where the intensity is to be considered. The analytical expression of the law is

$$I = V \cdot C = \frac{V}{R}, \qquad 208$$

where I is the intensity, V the p.d., C the conductivity, and R the resistance.

Faraday's law states *that the quantities of different elements set free by the same quantity of electricity are in the proportion of their atomic weights, divided by their valencies; and the quantities of different radicals set free by the same quantity of electricity are, in the proportion of their molecular weights, divided by their valencies.* In short, *the same quantity of electricity sets free equivalent quantities of elements or radicals.*

The analytical expression of the law is

$$\epsilon = 96537\,\eta, \qquad 209$$

where ϵ is the quantity of electricity in coulombs, and η is the valency. For 0.0_41036 grams of hydrogen correspond to 1 coulomb; and so 96537 coulombs correspond to 1 gramequivalent of hydrogen, that is, to 1 gram of hydrogen.

Joule's law states that *the quantity of heat produced by a current of electricity in passing through a conductor is proportional to the square of the intensity of the current.*

Its analytical expression is

$$Q = I^2B = \frac{IV}{R}B = IVCB = \frac{V^2}{R^2}B = V^2C^2B, \qquad 210$$

where B is a constant depending upon the units. When c.g.s. units are used, $B = 1$.

Problem.

Deduce this law from the principle of the conservation of energy.

89. **Ions.** — Let a and b of Fig. 14 be two plates of inert material dipping into a solution of some metallic salt. Charge a with + electricity, b with − electricity, by connecting with some source of electricity. The charges on a and b are at once more or less completely removed by the solution. We say the solution conducts electricity, but it is more in accordance with fact only to say that the electricity is removed from the plates. Is this power of removing electricity already in

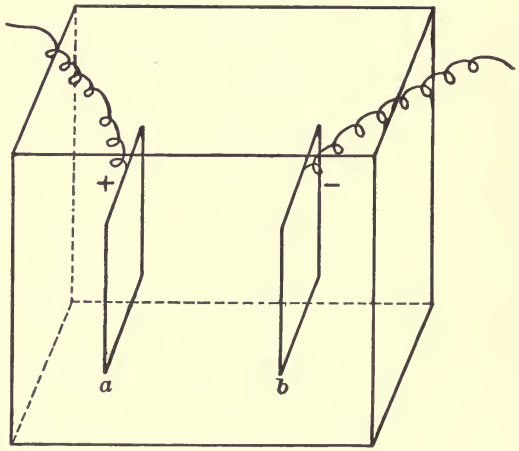

FIG. 14.

the solution before the plates are charged, or does the charging of the plates give rise to it? If the power is in the solution before charging, none of the electrical energy is needed to prepare the solution for action, and so the energy involved in the disappearance of the electric energy must be completely accounted for in the other actions. If the power is not in the solution before charging, some of the electrical energy is needed to prepare the solution for action, and so the energy involved in the disappearance of the electric energy cannot be completely accounted for in the other actions.

Very careful experiments in this direction indicate that solutions of metallic salts possess the power of absorbing electricity before electricity is added.

This belief gives rise to the ionic theory. An ion is an independent particle in a liquid. It is charged with either + or − electricity, never with both. No ion is known which is sometimes + and sometimes −. The sign of the charge on the ion *seems* to be as characteristic and as unalterable as the atomic weight. The ion is an electrically active independent particle, and this electrical activity is the essence of an ion. The instant the particle ceases to be electrically active, that instant the particle ceases to be an ion. The ionic condition is shown by a + sign or by a · for the positive ion, and by a − sign or by a ′ for the negative ion, the number of signs showing the number of ϵ_0 charges on the gramion, where

$$\epsilon_0 = 96537 \text{ coulombs.} \qquad 211$$

The + ions are called cations because + ions pass to the + electrode, which is called the cathode, and − ions are called anions because − ions pass to the − electrode, which is called the anode.

Any liquid which conducts electricity, or better absorbs electricity, does so by virtue of the ions it contains.

The conductivity of electricity by metals is an entirely different matter. We shall not consider that matter at all.

Very few pure liquids seem to contain more than a trace of ions. Consequently, very few pure liquids have more than a trace of conducting or absorbing power for electricity. Water is very slightly decomposed into ions; pure hydrochloric acid, not solution of it in water, and stannic chlorid, do not appear to be decomposed into ions at all.

Solutions of carbon compounds, not of the type MR, such as benzene, carbon tetrachlorid, etc., seem to be not at all decomposed into ions.

Solutions of all bodies of the type MR, on the other hand,

seem to be decomposed into ions; some very largely so decomposed, others less so, but all somewhat decomposed into ions.

This is particularly the case for aqueous solutions. In other solvents, the decomposition into ions is not so great.

The decomposition of a solute into ions is represented thus;

$$MR = (1 - x)\,MR + x\overset{+}{M} + x\overset{-}{R}. \qquad 212$$

Such a decomposition is called an ionic decomposition, ionic dissociation, or electrolytic dissociation.

The laws of equilibrium are as true for ionic decompositions as for other decompositions.

When we speak of an ion as being an independent particle, we mean this only in the sense that an ion can *move* independently of any other ion; we do not mean that it is independent in the sense that it is not under the influence of other ions. On the contrary, it is dependent on other ions in the sense that, except in most minute quantities, every + ion must have a corresponding − ion in its immediate vicinity. The charges on the ions are so enormous that were this not so, our ordinary chemical operations would be accompanied by most stupendous electric storms. A charge of 0.0007 coulombs changes the potential of a conducting sphere of the size of the earth one volt. One gram of $\overset{+}{H}$ has a charge of 96537 coulombs, so it is evident that were 96537 coulombs in a liquid without a corresponding quantity of − electricity, the electric disturbance would be tremendous.

However, very minute quantities of either + or − ions are often present without corresponding quantities of the other ion. This is what gives rise to potential differences in chemical changes. Leaving such cases out of account, we have as a rule to guide us that equal quantities of + and − charges appear together.

90. **Conductivity or absorption of electricity by solutions.** — Imagine the cell of Fig. 14 contains an aqueous solution of

HCl. Leaving out of account the minute quantity of $\overset{+}{H}$ and $\overset{-}{OH}$ from the water, we have available for absorbing electricity at the plates or electrodes, a and b, the ions $\overset{+}{H}$ and $\overset{-}{Cl}$, for

$$HCl = (1 - x)\,HCl + \overset{+}{H} + \overset{-}{Cl}.$$

Before the plates are charged, these ions are evenly distributed throughout the solution; but so soon as a is positively charged, and b negatively, a separation begins. A stream of $\overset{+}{H}$ sets in towards b, while a stream of $\overset{-}{Cl}$ sets in towards a. This directive or coördinate motion of the ions in the liquid produces the effect of a current of electricity in the liquid, and gives the impression of a passage of electricity from one electrode to the other. We see just how far this impression is correct. In time a is covered with anions, and b with cations, more electricity flowing to the electrodes from the source as the electricity on the electrodes is inductively neutralized by the electricity of the ions.

When the p.d. between a and b is small, nothing else of importance happens, the electricity on the electrode being inductively neutralized by the ions until the electrodes are covered up by the ions. We say inductively neutralized, because, as no body separates at the electrodes, the ions are still there as such, and therefore cannot have lost their charges. The neutralization, therefore, corresponds to the neutralization of a charged sphere brought close up to another charged sphere whose charge is of opposite sign, but kept beyond sparking distance.

The electrodes are said to be polarized; a is said to be anodically polarized; b cathodically polarized.

It is very probable that once in a while an ion passes away from the electrode and reacts with another ion with opposite charge. In this way there may be a small loss of electricity at each electrode, and an apparent current. Such an apparent current is called a convection current.

When the p.d. between *a* and *b* is not small, but is greater than a certain minimum value, then we get one of the most remarkable and puzzling changes known to science.

At *a* chlorin passes off and at *b* hydrogen passes off, and this continues so long as the p.d. does not drop below the minimum value referred to.

Only the ions are supposed to directly produce the free hydrogen and chlorin, so that, as $2\overset{+}{H}$ and $2\overset{-}{Cl}$ change into H_2 and Cl_2, the HCl furnishes fresh $\overset{+}{H}$ and $\overset{-}{Cl}$.

The hydrogen and chlorin escape as ordinary H_2 and Cl_2, without a sign of electric charge. As $\overset{+}{H}$ always has a + charge and $\overset{-}{Cl}$ always a − charge, it seems as if H is incapable of receiving a − charge to neutralize the + charge, and as if Cl is incapable of receiving a + charge to neutralize the − charge. So it is hard to account for the neutral molecule. On the other hand, we must remember all we really can say is that the *conditions are such* that when H and Cl ions are formed the + charge is invariably with the H and the − charge invariably with the Cl, but not that H *by its nature* can never be charged with − electricity, nor Cl by its nature with + electricity. So it is not at all inconsistent with observation to claim that when neutral H_2 is produced, it is neutral on account of equal charges of + and − electricity; one-half of the electricity on $\overset{+}{H}$ is exchanged for an equal quantity of − electricity. This seems preferable to claiming that one atom in the neutral H_2 molecule is + and the other atom −, for we thereby imply a difference in the two atoms which is not justified by observation.

A very serious difficulty in the ionic theory is the accounting for the formation of the ions. Gaseous H and Cl combine to form gaseous HCl with *loss* of energy to the system, so it is hard to see how ions can be formed in this operation. Passed into water, HCl dissolves with *further loss* of energy, so it is just as hard to account for the formation of ions in this opera-

tion. Of course, the student understands that to separate + and − electricities, as is done when ions are formed, needs energy. Until this matter is cleared up the theory will be subject to just criticism. But we should not be disturbed by this weakness in the theory, for it has already suggested so much to us and explained so many things that we may trust to the future for a satisfactory explanation of all difficulties.

91. Cause of the ionic state. — Believing that bodies do separate into ions, and that the energy needed for this is obtained in some way, why do they not entirely separate into ions? We may assume that all bodies separate into the smallest possible particles consistent with the conditions to which they are subjected, or else that bodies aggregate into the largest possible masses consistent with the conditions to which they are subjected. The first assumption is considered the better one; the phenomena of diffusion favor it.

In terms of energy, we say that the potential of volume energy, the pressure, tends to become equally distributed throughout space, so that the separation of a body into the smallest possible particles is a natural procedure. The energy needed for the volume energy of the ions as well as the space energy of electrical attraction between the ions, is gotten in some way we do not understand, but which we considered above.

Imagine two plates, a and b in Fig. 15, a certain distance apart in air, and each plate charged with a certain quantity of electricity ϵ. There is a certain p.d. between the plates, call it V. Replace the air by water, but do not change the distance between the plates. Then we find that V drops to about 1/75th of its previous value. So the *specific inductive capacity* or *dielectric constant* of water is about 75. The dielectric constants of all

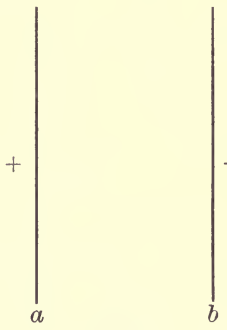

Fig. 15.

other solvents hitherto examined is much less than that of water; from about 1.8 for carbon disulfid to 33 for methyl alcohol. The high dielectric constant of water may be due to the hydrogen it contains. It would be interesting to determine the dielectric constant of liquid ammonia. But if the p.d. between two given charges of electricity is less in water than in any other liquid, the attraction between the charges is less, and consequently we expect to find a greater ionic decomposition in water than in any other solvent. This is the case. More bodies are decomposed in water, and to a greater extent, than in any other solvent. Curiously, as before stated, water itself is hardly at all decomposed ionically.

But the solutes are never completely ionized. The relation between ionized and not ionized parts follows the general law of equilibrium, so that ionisation and other decompositions are similar in their origin.

92. **Measuring the electric conductivity or absorption of electricity by solutions.** We cannot go into detail; that must be sought in works on electricity. It is obvious that for accurate results, the neutralized ions must not be allowed to cover up the electrodes at which the absorption is to take place. This is prevented by reversing the potentials of the electrodes very rapidly, so that opposite ions pass each successive moment to the electrodes and react with the ions previously there, to form the initial body back again. In this way we can get the quantity of electricity absorbed in unit time with great accuracy. Unfortunately the results are commonly expressed in terms of conductivity, just as if a certain quantity of electricity had passed from one electrode to the other through the liquid. Of course the numerical result is the same, for in respect to numerical value, it makes no difference whether a unit of electricity disappears from an electrode, because an equal quantity of the opposite electricity has been brought all the way from the other electrode or whether it has been absorbed by the electricity on ions which may never have been in con-

tact with the other electrode. But in idea the two expressions are fundamentally different.

The absorption evidently depends upon the area of the electrodes and upon the distance between them. We therefore agree to refer the results to a vessel whose parallel electrodes have each an area of 1000 cm^2, are at a distance of 1 cm. apart, and have a p.d. of 1 *V*. So 1000 cc. of solution can be contained between them. This is the standard conductivity cell.

The conductivity of a solution divided by the conductivity of an equal volume of mercury and of the same geometric form is called the *specific conductivity* of the solution. When the conductivity is computed for a grammolecule in 1000 cc. solution, it is called the molecular conductivity, and is denoted by μ. The molecular conductivity is obtained for any concentration by multiplying the given conductivity at that concentration by the reciprocal of the concentration expressed in grammolecules per liter solution. The equivalent conductivity refers to gram-equivalents per liter.

Usually the determination of μ is made by comparing with an ohm or a mercury unit of resistance. The value so obtained must be multiplied by $1000 \cdot 100 \cdot 100/1.06 = 10^7/1.06$ to get the specific conductivity in the standard cell when an ohm is the unit, or by 10^7 when a mercury unit is the unit.

Problem. — Why?

Example. — The specific conductivity of an aqueous solution of KCl 1/50th normal is $0.0_6 2379$ mhos at a certain temperature; hence its conductivity in the standard cell is

$$\frac{0.0_6 2379 \cdot 10^7}{1.06} = 2.244 \text{ Hg units,}$$

and

$$\mu = \frac{2.244}{\left(\frac{1}{50}\right)} = 112.2.$$

This means that a normal aqueous solution of KCl between electrodes of standard size and arrangement, and a p.d. of 1 *V*

between them, *provided it retains the absorptive power that it has at 1/50th normal*, absorbs 112.2 coulombs per second at the temperature of the measurement.

Problems.

1. A 5 % aqueous solution of KCl at 0° has a specific conductivity of 0.0_56617 mhos. What is μ? *Ans.* $\mu = 93$.

2. One grammolecule of KCl is dissolved in 100 liters solution. Specific conductivity $= 0.0_61216$ mhos. What is μ? *Ans.* $\mu = 114.7$.

3. For a solution of KCl in H_2O, $\mu = 106.8$, and the specific conductivity $= 0.0_51132$ mhos. One grammolecule KCl is therefore dissolved in how many liters H_2O. *Ans.* 10 liters.

93. **Migration of the ions.** — From what has been said, the student sees that the absorptive power of a solution for electricity depends upon the speed with which the ions travel towards the two electrodes. If two solutions are given of the same molecular concentration in the same solvent, and each ion of one solution moves twice as fast as the corresponding ion of the other solution,

$$\mu_1 = 2\,\mu_2.$$

Let ϵ_0 (= 96537 coulombs) be the electricity on each gramion when monovalent; when polyvalent, consider a gramequivalent of the ion. Then, the total quantity of electricity passing through the electrodes in a second at 1 V p.d., in normal solution, is

$$\mu = \epsilon_0 a + \epsilon_0 b = \epsilon_0 (a + b), \qquad 213$$

where a and b are the velocities of the two ions. We assume the ions move independently of each other. This is probably so because the theoretical results obtained by assuming this agree well with experimental data.

The velocities a and b are computed in the following way:

Suppose we have 16 grammolecules of a salt in 1000 cc. solution, and let each $\pm$ of Fig. 16 represent a grammolecule. Imagine that this diagram intervenes between the electrodes of Fig 14, and that in this particular case a non-alternating current decomposes the salt in solution. Any free $-$ on the left of Fig. 16 represents a gramion deposited on a; similarly,

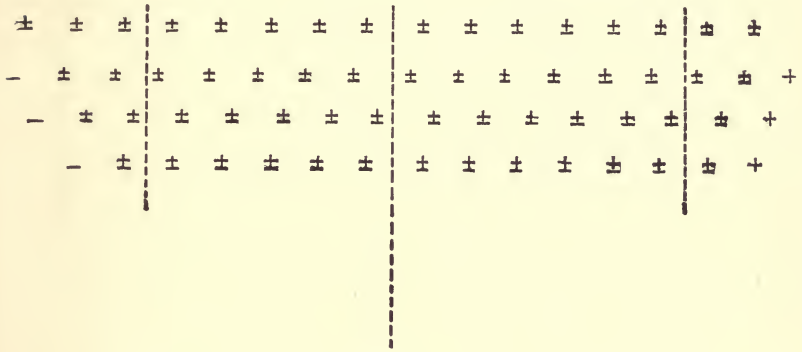

Fig. 16.

any free $+$ on the right of Fig. 16 represents a gramion deposited on b. Let u and v refer to cation and anion respectively, and let them represent the distances traveled by the ions in opposite directions until

$$u + v = 1.$$

Suppose that this unit distance is the distance between two adjacent vertical columns of $\pm$. Suppose $u = 2v$. Then at the end of a certain time we shall have the condition of affairs represented by the second horizontal line, the first horizontal line of course representing the initial condition. Every cation has moved a certain distance to the right toward the cathode, while every anion has moved half that distance toward the anode. This is supposed to continue so long as we choose,

but for the purpose it is sufficient to consider the operation finished when the grammolecules have reached the same position in regard to the verticals that they had at the outset.

We started with 16 grammolecules. We have 13 grammolecules left; so 3 grammolecules have been decomposed. But whereas the concentration at the outset in each half of the vessel was the same, at the end the concentration is diminished less on the side toward which the faster ion migrated than on the other side toward which the slower ion migrated. In this case the greater concentration is around the cathode. The cation is the faster ion. The solution in the anode half has lost 2 grammolecules, while that in the cathode half has lost only 1 grammolecule. So *the relative loss in concentration in each half of the solution electrolyzed gives the relative velocities of the ions.* These values we shall denote by u for cation and v for anion, as before stated. We see that u and v denote the distance each ion migrates in opposite directions, until there is unit distance between them. In this particular case, $u = 0.67$, $v = 0.33$. Many writers put $u = n$ and $v = 1 - n$; others, $u = 1 - n$, $v = n$. The quantities u and v are called the migration values of the ions, or the Hittorf constants, from Hittorf, who first investigated this matter thoroughly.

The student should clearly understand that this matter of the migration constants is a theoretical matter. All we know is that the concentration of a solution around the electrodes changes during electrolysis in an unequal way. This is the fact. The migration values of the ions is the theoretical explanation of this fact.

For the experimental determination of u and v, we cannot divide the vessel into partitions unit distance apart, so we let the total quantity of either ion set free represent the total distance between the ions, and then the relative change in concentration gives the fraction of that distance traversed by each ion. The student can see from Fig. 16 that it is not necessary to analyze each whole half of the solution, but

only to take so much of it around each electrode as to get all that part which could possibly have changed in concentration. The dotted lines near each end show how much we should take in this particular case. Details must be sought elsewhere.

EXAMPLE. — An aqueous solution of $CuSO_4$ is the solution; quantity of Cu deposited on cathode is 0.2955 grams. Electrodes of inert material. A certain volume around the cathode contained 2.2762 grams Cu before electrolysis; the same volume contains 2.0650 grams Cu after electrolysis. There is therefore a loss in the solution of 0.2112 grams Cu while 0.2955 grams Cu are deposited. Hence $0.2955 - 0.2112 = 0.0843$ grams Cu have migrated to the cathode, and $u = 0.0843/0.2955 = 0.285$, $v = 1 - u = 0.715$.

The same result would have been obtained had the solution around the anode been analyzed.

PROBLEMS.

1. From the following data calculate u and v. Electrodes of inert material.

Solution in H_2O.	Quantity Ag dep.	Certain vol. around cathode gave: Before decomp.	After it.
$AgNO_3$.	1.2590 grams.	17.4600 grams AgCl;	16.6800 grams AgCl.
Ag_2SO_4.	0.1099 "	0.4166 " "	0.3358 " "
$AgC_2H_3O_2$.	0.2197 "	0.3736 " "	0.2631 " "

Ans. For $AgNO_3$ $u = 0.53$, $v = 0.47$.
" Ag_2SO_4 $u = 0.45$, $v = 0.55$.
" $AgC_2H_3O_2$ $u = 0.62$, $v = 0.38$.

2. Electrodes of Cu. Solution of $CuSO_4$ in H_2O. Quantity of Cu deposited on cathode = 0.2294 grams. 32.36 grams solution around the anode contained 1.195 grams Cu before electrolysis; after electrolysis, 32.78 grams solution around the anode contains 1.360 grams Cu. What are u and v?

Ans. $u = 0.28$, $v = 0.72$.

3. Electrodes of inert material. Solution of $K_2Cr_2O_7$ in H_2O. Current passed through a voltmeter in circuit deposited 1.442 grams Ag. Before electrolysis 9.299 grams solution around the anode gave 0.3459 grams Cr_2O_3. After electrolysis 23.30 grams solution gave 0.7263 grams Cr_2O_3. What are u and v? *Ans.* $u = 0.54$, $v = 0.46$.

The migration values of the ions vary somewhat with the concentration of the solution. Likewise with the temperature somewhat, not very much. The effect of temperature varies with the ions, but seems, on rising, to bring all migration values towards 0.5, increasing those below 0.5 and decreasing those above 0.5.

94. **Absolute velocity of the ions.** — The migration values of the ions are only relative values, but so soon as we know the molecular conductivity of a solution, we know the total quantity of electricity that is absorbed by the ions per second, and therefore we can find how fast they must move up to the electrodes to do this.

Example. — The molecular conductivity of an aqueous solution of HCl is 363. Each gramion of $\overset{+}{H}$ or $\overset{-}{Cl}$ carries 96537 coulombs, but as only 363 coulombs are absorbed by the solution per second, it follows that the gramions get separated by only 363/96537 cm. per second, for the electrodes of the standard cell are 1 cm. apart. Hence $\overset{+}{H}$ and $\overset{-}{Cl}$ travel apart at the rate of $363/96537 = 0.00376$ cm. per second. The migration value of $\overset{+}{H}$ in HCl solution is $0.83 = u$, that of $\overset{-}{Cl}$ in HCl solution is $0.17 = v$. Hence 0.00376 cm. is to be divided proportionally to these quantities; namely, 0.00312 cm. and 0.0_364 cm. per second, and these are the respective velocities of $\overset{+}{H}$ and $\overset{-}{Cl}$ *in any solution.*

PROBLEMS.

1. For KOH solution at 18°, $u = 0.26$, $\mu = 186$. What are the velocities of $\overset{+}{K}$ and $\overset{-}{OH}$?

Ans. $\overset{+}{K} = 0.0_353 \frac{\text{cm.}}{\text{sec.}}$; $\overset{-}{OH} = 0.00151 \frac{\text{cm.}}{\text{sec.}}$.

2. For NaI solution at 25°, $u = 0.374$, $\mu = 119$. What are the velocities of $\overset{+}{Na}$ and $\overset{-}{I}$?

Ans. $\overset{+}{Na} = 0.0_349 \frac{\text{cm.}}{\text{sec.}}$; $\overset{-}{I} = 0.0_382 \frac{\text{cm.}}{\text{sec.}}$.

3. For $ZnSO_4$ solution at 18°, $u = 0.32$, $\mu = 212$. What are the velocities of $\overset{+}{Zn}$ and $\overset{-}{SO_4}$?

Ans. $\overset{+}{Zn} = 0.0_335 \frac{\text{cm.}}{\text{sec.}}$; $\overset{-}{SO_4} = 0.0_374 \frac{\text{cm.}}{\text{sec.}}$.

95. **Conductivity or absorption in terms of velocity.** — We see from 213 how to get μ from the absolute velocities when the solute is completely ionized. When the solute is not approximately completed ionized, the observed or computed μ is referred to the ionized part only. In the preceding problem the solute is supposed to be completely ionized. As the ionized part only is active in absorbing electricity, when the degree of ionisation given $= x$, it is easy to apply a correction and find μ for any concentration for which x is given.

PROBLEMS.

1. How would you do this?

2. Assume $x = 1$, velocity of $\overset{+}{NH_4} = 0.0_362 \frac{\text{cm.}}{\text{sec.}}$, that of $\overset{-}{Cl} = 0.0_364 \frac{\text{cm.}}{\text{sec.}}$. What is μ for NH_4Cl? *Ans.* $\mu = 122$.

3. Assume $x = 1$, velocity of $\overset{+}{Ag} = 0.0_361 \frac{\text{cm.}}{\text{sec.}}$, that of $\overset{-}{C_2H_3O_2} = 0.0_338 \frac{\text{cm.}}{\text{sec.}}$. What is μ for $AgC_2H_3O_2$?

Ans. $\mu = 96.5$.

In general, instead of using the absolute velocities, the quantities $\epsilon_0 a$ and $\epsilon_0 b$ are determined once for all from a few values of μ, and tabulated so that when a conductivity is desired, the proper $\epsilon_0 a$ and $\epsilon_0 b$ are selected and their sum gives μ *when* $x = 1$ *nearly or quite.* The quantities $\epsilon_0 a$ and $\epsilon_0 b$ are generally denoted by U and V respectively, so that

$$\mu = U + V, \qquad 214$$

and

$$u = \frac{U}{U+V}, \quad v = \frac{V}{U+V}. \qquad 215$$

96. **Conductivity or absorption and concentration.** — We have adopted the theory that the absorption of electricity is effected by the ions. We have also adopted the theory that ionisation follows the same law that expresses the incomplete decomposition of any body, when the products form an equilibrium with the initial body. Theory and experiment show that whenever the products of such a decomposition occupy a larger volume than the initial body, a change in volume or of pressure produces a change in the decomposition. Hence μ should change when π, the osmotic pressure, or when c, the concentration, changes. Not only this, but the change in μ should follow the law of equilibrium. The velocities of the ions do not seem to be wholly independent of the concentration, but the change in this respect is so slight that in comparison with the change due to alteration in concentration, in a first approximation at any rate, it may be neglected. The equation of equilibrium, in the case of ionisation, is

$$K = \frac{x^2}{(1-x)v}, \qquad 216$$

for

$$MR = (1-x)MR + xM + xR.$$

From 216, x can only equal 1 when $v = \infty$ and, therefore, the maximum value of μ, that is μ_∞, cannot be observed directly. As the molecular conductivity is directly proportional to the

degree of ionisation, and when $x = 1$, the molecular conductivity reaches its highest value $= \mu_\infty$, we may put

$$x = \frac{\mu}{\mu_\infty}, \qquad 217$$

where μ is the molecular conductivity corresponding to x. Substituting in 216,

$$K = \frac{\left(\frac{\mu}{\mu_\infty v}\right)^2}{\frac{\left(1 - \frac{\mu}{\mu_\infty}\right)}{v}} = \frac{\mu^2}{(\mu_\infty - \mu)\mu_\infty v}, \qquad 218$$

from which K and μ_∞ can be computed when μ and v are determined for two different concentrations. This equation expresses the relation with remarkable accuracy in some cases; in other cases it fails lamentably: possibly the velocities of the ions change with concentration more than we think. But it is so accurate in so many cases that it is not easy to reject it and the reasoning which led to it.

Some modifications of 218 have been proposed. Multiply by $\sqrt{v}$, so that

$$K_1 = \frac{\left(\frac{\mu}{\mu_\infty} \cdot \frac{1}{v}\right)^2 \sqrt{v}}{\left(1 - \frac{\mu}{\mu_\infty}\right)\frac{1}{v}} = \frac{\left(\frac{\mu}{\mu_\infty}\right)^2}{\left(1 - \frac{\mu}{\mu_\infty}\right)\sqrt{v}} = \frac{\mu}{(\mu_\infty - \mu)\mu_\infty \sqrt{v}}. \qquad 219$$

Modifying this a little,

$$K_2 = \frac{\left(\frac{\mu}{\mu_\infty} \cdot \frac{1}{v}\right)^{\frac{3}{2}}}{\left(1 - \frac{\mu}{\mu_\infty}\right)\frac{1}{v}} = \frac{\left(\frac{\mu}{\mu_\infty}\right)^{\frac{3}{2}}}{\left(1 - \frac{\mu}{\mu_\infty}\right)\sqrt{v}} = \frac{\left(\frac{\mu}{\mu_\infty}\right)^3}{\left(1 - \frac{\mu}{\mu_\infty}\right)^2 v} = \frac{\left(\frac{\mu}{\mu_\infty} \cdot \frac{1}{v}\right)^3}{\left[\left(1 - \frac{\mu}{\mu_\infty}\right)\frac{1}{v}\right]^2}.$$

Extracting the cube root of the last member,

$$K_3 = \frac{\frac{\mu}{\mu_\infty} \cdot \frac{1}{v}}{\left[\left(1 - \frac{\mu}{\mu_\infty}\right)\frac{1}{v}\right]^{\frac{2}{3}}}, \qquad 220$$

or

$$\frac{K_3}{\left[\left(1 - \frac{\mu}{\mu_\infty}\right)\frac{1}{v}\right]^{\frac{1}{3}}} = \frac{\frac{\mu}{\mu_\infty} \cdot \frac{1}{v}}{\left(1 - \frac{\mu}{\mu_\infty}\right)\frac{1}{v}}. \qquad 221$$

The denominator of the first member is the cube root of the concentration of the non-ionized part of the solution, its reciprocal is therefore a measure of the distance between the particles of the solute. The numerator of the second member is the concentration of the ionized part of the solute; the denominator of the second member is the concentration of the non-ionized part. So 221 states that the ratio of the concentrations of the ionized and non-ionized part of the solute is proportional to the distance between the particles of the non-ionized part of the solute. Equations 219 and 220 do express the results of experiment better in many cases than 218, but they have the disadvantage of being almost purely empirical. We hardly believe that 218 is really wrong in principle.

The electrical conductivity is easily measured, and is therefore a valuable means for finding the degree of ionisation $= x$ or the constant of ionisation $= K$. The K used in connection with fractional precipitation was found in this way.

Example. — Suppose we are to find x for benzoic acid in 1/10th normal aqueous solution. We find μ by experiment at that concentration, and can get μ_∞ from 218 after two separate observations. It is better, however, to get μ_∞ thus. Salts of the alkalies, salts of Ag and of Tl, with monovalent acid radicals, are very much ionized in aqueous solution, even in ordinary dilute solutions; so that μ_∞ can be computed from observations on solutions not so dilute that impurities in the water and

errors of measurement cause serious error in the value of μ_∞. It is obvious, from the form of 218, the μ and μ_∞ should be as wide apart as possible. Let the salt in this case be sodium benzoate. Subtracting the part of μ_∞ due to $\overset{+}{\mathrm{Na}}$, the balance, after adding that due to $\overset{+}{\mathrm{H}}$, gives μ_∞ for benzoic acid. It is then easy to find x with 218 and 217 for 1/10th normal aqueous solution.

Problems.

1. For *m*-acetamidobenzoic acid, $K = 0.0_485$, $\mu_\infty = 350$. What is μ at 1/256th normal aqueous solution? *Ans.* $\mu = 44.1$.

2. For acetosalicylic acid, $C_6H_4(OCOCH_3)COOH$, in aqueous solution, $\mu_\infty = 351$; $v = 64$, $\mu = 48.4$; $v = 128$, $\mu = 65.7$; $v = 256$, $\mu = 88.6$; $v = 512$, $\mu = 117.2$; $v = 1024$, $\mu = 151.5$. What is the average value of K? *Ans.* $K = 0.0_33$.

3. For vanillic acid, in aqueous solution, $\mu_\infty = 354$, $K = 0.0_4298$, $v = 512$. What is x? *Ans.* $x = 0.11$.

4. For water at 18°, $\mu = 0.0361 \cdot 10^{-3}$; U = 290, V = 165. What is the concentration of the water ions, $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{OH}}$? In solving this problem, assume that one grammolecule of water is dissolved in the liter.

Ans. The one grammolecule H_2O contains $8 \cdot 10^{-8}$ gramions each of $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{OH}}$. This is the quantity of ions in the liter of H_2O.

97. **Temperature and conductivity or absorption.** The conductivities of metals diminish as T increases, but the absorption by bodies in solution sometimes increases, sometimes decreases as T increases. This is easily explained. We saw on page 170 that the migration values of the ions seemed to approach a common value 0.5. Similarly we find in many cases an approach of the temperature coefficient of electric conductivity, or of absorption, to the common value 0.022.

The *temperature coefficient* is a quantity which shows the change in conductivity or absorption for 1°, in terms of some other conductivity or absorption taken as a unit. The conductivity or absorption at 18° is usually the unit. So if β is the coefficient,

$$\beta = \frac{\mu_t - \mu_{18}}{(t-18)\,\mu_{18}}. \qquad 222$$

For all acids β seems to diminish with rising temperature, but this is not true for salts.

Probably in all cases the velocity of the ions increases with T, so that were there no other action, β would always be positive and probably have the value 0.022. But there is another action; namely, the ionic decomposition. Letting K be the constant of ionisation,

$$K = \frac{c'^2}{c},$$

and from 201,

$$\frac{d}{dT}\left(lK\right) = \frac{Q}{RT^2}, \qquad 223$$

where Q is the heat of ionisation. When Q is $+$, that is when Q is absorbed in producing ions, $d(lK)/dT$ is $+$, and so K and c' increase with T, and β is $+$. But when Q is negative, that is when heat is given out in producing ions, c' diminishes as T increases, so that a time comes when the increase in absorption due to increased velocity of the ions is balanced by decreased absorption due to diminished c', and so β passes from $+$ through 0 to $-$. Such cases are now well known, but they were not found until the ionic theory foretold them.

98. **Absorption by melted salts and solids.** — All melted salts seem to absorb electricity, and possibly all solid compounds do likewise, but the data are too meager to draw positive conclusions. Experiments seem to show that the addition of a solid salt to another solid salt increases the absorption power of the mixture for electricity, just as the analogy between liquid and solid solutions would lead us to expect.

99. **Force acting on the ions.** — The energy of moving 1 coulomb against 1 volt is 10^7 ergs. Under the force of 1 volt, 96357 coulombs travel through 0.00312 cm. per second as $\overset{+}{\mathrm{H}}$. Since

$$fv = W,$$

where f is force, v velocity, W work, we have as the force needed to give a gramion of $\overset{+}{\mathrm{H}}$, a velocity of 1 cm. per second

$$f = \frac{96537 \cdot 10^7}{0.00312} = 309 \cdot 10^{12} \text{ dynes.}$$

Similarly for other ions. The force is enormous, but not unreasonably large in view of the extreme minuteness of the particles.

100. **Cause of potential difference.** — When one body is brought in contact with another body of different nature, and then the two separated, they are found to have a p.d. The cause of this separation of electricity has been under dispute for years, and the dispute is not yet concluded, though our ideas on the subject are getting clearer. When both bodies are solid, the matter seems to be much more obscure than when one body is a liquid. Probably the cause is the same in each case, but the difficulties in the examination of all solid systems have not yet been overcome, and so we shall not dwell on this part of the subject, but pass right on to systems which contain one or more liquids.

101. **Chemical and electrical energy.** — Chemical energy is defined as that energy which is the cause of chemical action. But in chemical action we meet only heat, light, electricity, mechanical energy, or some other well-known energy. So the assumption of chemical energy is strictly gratuitous and not to be advised at all. It is far better to consider electricity as the cause of chemical activity, for by so doing we can express chemical action in terms of a well-defined energy, instead of in terms of the vague chemical energy. Moreover, we find

that the chemical activity of a body is closely connected with the electric energy the body can produce. If A and B react separately with C, and A in the reaction develops E_1 units of electric energy, while an equivalent quantity of B develops E_2 units of electric energy, where $E_2 > E_1$, B will react with C to the greater or less exclusion of A, though never complete exclusion of A. Hence it is very important for the chemist to know the electric energy involved in a chemical change.

It was formerly supposed that heat energy held this relation; that is, that the quantity of heat evolved in a reaction measured the chemical activity of the reacting bodies, but later investigation did not favor this idea. In a general way, heat energy and chemical energy go together, but when the difference in the heat of two reactions is slight, heat energy fails to indicate which reaction will take place, and it fails sometimes indeed when the difference is great.

The electric energy held a subordinate place as a criterion of chemical action, heat energy holding the first place. The electric energy was supposed to come from the heat energy. Consequently when Q heat units were produced in a certain reaction, it was believed that we could get $42750 \cdot 981 \cdot Q$ c.g.s. units of electricity. In volts and coulombs, assuming the reaction is expressed in gramequivalents, that is in quantities which contain $\epsilon_0 = 96537$ coulombs,

$$V\epsilon_0 = \frac{42750 \cdot 981 \cdot Q}{10^7},$$

or

$$V = \frac{42750 \cdot 981}{96537 \cdot 10^7} Q = 0.0_4 4339\, Q, \qquad 224$$

where V = p.d. in volts, and Q refers to the chemical equation expressed in gramequivalents. When the chemical equation is in the ordinary form, to find V we must divide Q by the valency involved.

We now know that 224 is not correct; sometimes V is greater,

sometimes less than it should be by that equation. Besides, 224 is not in accord with the second law of thermodynamics.

From the first law,

$$Q = W + U, \qquad 225$$

where Q is now the *total available heat*, W the available energy, in this case appearing as electric energy E, and U the change in *internal* energy, in this case appearing as the heat of the chemical reaction. Substituting in 42, we have

$$dE = (E + U)\frac{dT}{T},$$

or

$$E = -U + T\frac{dE}{dT}. \qquad 226$$

By condition, the capacity factor ϵ_0 is constant, and putting for U the proper symbol Q, not the same Q as in 225, we have

$$V\epsilon_0 = -Q + T\epsilon_0\frac{dV}{dT}, \qquad 227$$

or

$$V = -\frac{Q}{\epsilon_0} + T\frac{dV}{dT}. \qquad 228$$

Example. — In the Daniell cell Zn replaces Cu; that is,

$$Zn + CuSO_4aq = ZnSO_4aq + Cu - 50100 \text{ cals.}$$

aq after a symbol means water of solution, often an indefinite quantity. So from 224,

$$V = 0.0_4 4339 \cdot \frac{50100}{2} = 1.09;$$

the observed $V = 1.10$, a good agreement.

Problems.

1. $Zn \mid H_2SO_4 + 100\,H_2O \mid CdSO_4$ conc. sol. $\mid Cd = -16210$ cals. This means that metallic Zn, which forms one electrode, dips into a solution of 1 grammolecule H_2SO_4 in 100 grammolecules H_2O, which solution is in contact with a concentrated solution

of $CdSO_4$, but not mixed with it, the two solutions being separated either by a porous diaphragm or by gravity. Metallic Cd dips into the $CdSO_4$ solution, forming the other electrode. When electric connection is made externally between the electrodes, Zn passes into solution, and Cd separates out. The + electricity is liberated at the electrode toward which the arrow points. The reaction liberates 16210 cals., and hence the − sign. What is V? *Ans.* $V = 0.35$; obs. $V = 0.35$.

2. $Zn + 2\,Cl + aq = ZnCl_2aq + H_2 + 112800$ cals.

$$Ag + Cl = AgCl + 29400 \text{ cals.}$$

$$Zn \mid 2\,HClaq \mid AgClAg.$$

When a term is written MR, M, it means that salt and metal are solid and in contact with each other. What is V?

Ans. $V = 1.17$; obs. $V = 1.16$.

3. $Cu + 2\,HNO_3Ag = Cu(NO_3)_2aq + 2\,H + 16100$ cals.

$$Ag + HNO_3 = AgNO_3 + H + 25900 \text{ cals.}$$

$$Cu \mid Cu(NO_3)_2\,aq \mid \overrightarrow{AgNO_3aq} \mid Ag.$$

What is V? *Ans.* $V = 0.779$; obs. $V = 0.43$.

In the last problem, it is very plain that the two energies are not equivalent. In some cases, indeed, the electric energy has turned out to be greater than the heat energy.

In the first two problems $dV/dT = 0$; in the third problem $dV/dT < 0$. When $E > Q$, $dV/dT > 0$.

Problems.

1. Suppose dV/dT is +, and consider the cell at several successively greater temperatures, what do you notice in

regard to E and Q? Suppose dV/dT is $-$, and T increases as before, what do you notice now in regard to E and Q?

2. Ag | $AgNo_3$ $\frac{1}{10}$ normal | KNO_3 $\frac{1}{10}$ normal | KCl $\frac{1}{10}$ normal | AgCl, Ag.

$$V \text{ at } 15° = 0.4433,$$

$$V \text{ at } 77° = 0.394.$$

Substituting Br for Cl,

$$V \text{ at } 16° = 0.6010,$$

$$V \text{ at } 77° = 0.5365.$$

Substituting I for Cl,

$$V \text{ at } 14.5° = 0.8165,$$

$$V \text{ at } 76.5° = 0.7585.$$

$$Ag + N + 3O + aq = AgNO_3aq - 23300 \text{ cals.}$$

$$K + N + 3O + aq = KNO_3aq - 111000 \text{ cals.}$$

$$Ag + Cl = AgCl - 29400 \text{ cals.}$$

$$Ag + Br = AgBr - 22700 \text{ cals.}$$

$$Ag + I = AgI - 13800 \text{ cals.}$$

$$K + Cl + aq = KClaq - 101200 \text{ cals.}$$

$$K + Br + aq = KBraq - 90200 \text{ cals.}$$

$$K + I + aq = KIaq - 75000 \text{ cals.}$$

What is the calculated V in each case?

$$V = 0.463, \quad 0.566, \quad 0.878.$$

The agreement with the observed V is not very good, but is better by far than that calculated from Q alone.

3. A cell is composed of

$$Hg, Hg_2SO_4 \mid Na_2SO_4 . 10\,H_2O \text{ moist} \mid Na_2SO_4 + 10\,H_2O \mid Hg_2SO_4 Hg.$$

In the following table the potential difference is given in volts at the corresponding temperatures:

+ 0.0375,	28.3°,	+ 0.0080,	31.8°.
+ 0.0229,	30.1°,	− 0.0006,	32.6°.

What is remarkable about this, and how is it to be interpreted?

What application could you make of the subject matter in this section to these data?

102. **Experimental measurement of V.**—The different methods of determining V must be sought in larger works. We mention one method; namely, by opposing to V a known p.d. as nearly as convenient equal to V, and measuring the remaining slight difference by a capillary electrometer. The known p.d. used in this way is commonly one of the following:

The Daniell cell;

$$Zn \mid ZnSO_4 \text{ sol.} \overrightarrow{\mid} CuSO_4 \text{ sol.} \mid Cu = 1.10\,V \text{ about.}$$

The Clark cell;

$$Zn \mid ZnSO_4 \text{ sol.} \overrightarrow{\mid} HgSO_4, Hg = 1.434\,V \text{ about.}$$

The Helmholtz cell;

$$Zn \overrightarrow{\mid} ZnCl_2 \text{ sol.} \mid HgCl, Hg = 1.00\,V \text{ about.}$$

The p.d. of these cells varies somewhat with the concentrations of the solutions, but for a given concentration the p.d. is strictly constant. A correction for T must be made.

To determine the p.d. of a cell, say,

$$Zn \mid ZnCl_2 \text{ sol.} \mid CuCl_2 \text{ sol.} \mid Cu,$$

we set up the arrangement of Fig. 17. C is a source of electricity sending a current through a circuit of known resistance. The p.d. at the electrodes of C is accurately known,

so the p.d. $= V_0$ between A and B can be accurately computed. Then assuming that AB has the same conductivity throughout, the p.d. between D and $B = V$ is the same part of V_0 that DB is of AB, or

$$V = \frac{DB}{AB} V_0.$$

The electrometer is at E, and the cell whose p.d. is to be measured is at X. Contact is made along AB until the electrometer shows little or no deflection, if the adjustment can be made so perfect; if not, the slight deflection of electrometer gives the necessary correction. Substituting in the

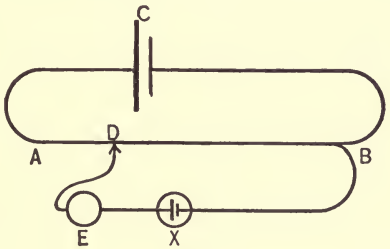

FIG. 17.

equation gives V. The value of V so obtained is the sum of the p.d. throughout the cell, and does not tell us anything about the parts of V. In the cell considered there may be a p.d. between Zn and $ZnCl_2$ sol., between $ZnCl_2$ sol. and $CuCl_2$ sol., between $CuCl_2$ sol. and Cu, and between Cu and Zn. When we know three of these potential differences, subtracting their sum from V is believed to leave the third one.

We get the p.d. between Zn and $ZnCl_2$ sol. as shown in Fig. 18. We cannot introduce a rod of Cu or any other solid conductor into the solution, to make electric connection with the electrometer, for this would introduce a new unknown p.d. But by using mercury and arranging so that the mercury runs out in a fine stream and breaks into globules just at the surface of the solution, it would seem that the mercury takes the same poten-

tial as the solution, though there is some dispute about this, and yet connects with the electrometer. So no new p.d. is introduced other than that between Zn and Hg. But careful experiment has shown that the p.d. between metals is very slight. Hence the p.d. observed in this way is probably very nearly the desired p.d. between Zn and $ZnCl_2$ solution.

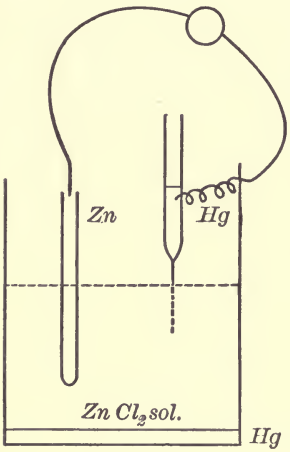

FIG. 18.

Another way would be to arrange as in Fig. 19. The jar on the left is as in the preceding. The solution is connected through a siphon, one limb of which is filled with the $ZnCl_2$ sol., the other limb with a normal aqueous KCl solution, and dips into an auxiliary cell containing a normal aqueous solution of KCl and Hg at the bottom covered with a layer of HgCl. The Hg is the other electrode. Connection is made with it by a Pt wire fused through the bottom. The p.d. of the auxiliary cell is $-0.56\,V$; that is, on passing from metal to solution, from Hg to KCl sol., the p.d. drops from $0\,V$ to $-0.56\,V$. This is determined once for all by a mercury dropping electrode. Assuming there is no p.d. between the two solutions $ZnCl_2$ sol. and KCl sol., we need only to subtract $+0.56\,V$, or add $-0.56\,V$, from the p.d. given by the electrometer to get the p.d. between $Zn\,|\,ZnCl_2$ sol. Sometimes the difference in specific gravity is sufficient to keep the solutions apart and the double U-tube may be dispensed with.

EXAMPLE. —

$$Zn\,|\,ZnSO_4 \text{ normal} \,\|\, KCl \text{ normal}\,|\,HgCl,\ Hg = 1.08\,V,$$

aqueous solutions. That is, starting with Zn at 0 potential to

$ZnCl_2$ normal to KCl normal to HgCl, Hg, there is a total rise of potential $= 1.08\,V.$ The last step is a step up of $0.56\,V.$ The preceding step from $ZnCl_2$ normal to KCl normal is just about on a potential level. So the first step must have been

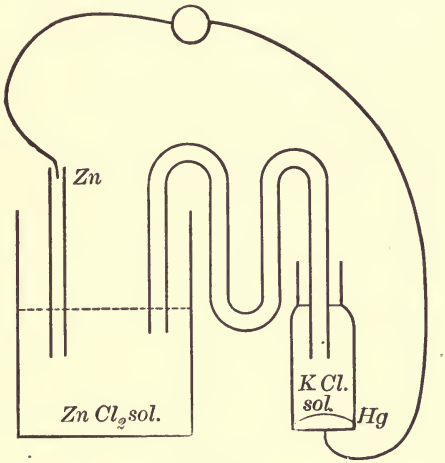

Fig. 19.

a step up of $0.52\,V.$ This is the desired p.d. between Zn | $ZnCl_2$ normal. The value is not quite exact, for, as we have said, there is a slight p.d. between the solutions and also between the metals. They are so slight they may be neglected, still it would not be difficult to make a proper correction.

Problems.

1. Cu | $CuSO_4$ normal $\overleftarrow{|}$ KCl normal | HgCl, Hg $= 0.025\,V.$

What is the p.d. of Cu | $CuSO_4$ normal? Aqueous solution.

Ans. p.d. $= -0.585\,V.$

2. Pt | H_2SO_4 normal $\overleftarrow{|}$ KCl normal | HgCl, Hg $= 0.75\ V.$

What is the p.d. of Pt | H_2SO_4 normal? Aqueous solution.

Ans. p.d. $= -1.31\ V.$

103. **Source of the electric energy.** — We have seen that the heat energy is not the only source of the electric energy, if it is ever the source at all. The only other source that seems possible is the osmotic energy.

Consider the combination M | MR; that is, a metal in a solution of one of its salts. The salt is ionized into $\overset{+}{\mathrm{M}}$ and $\overset{-}{\mathrm{R}}$. When the concentration of the cations is changed, energy is involved according to 13. Replacing ϕ by π,

$$W = RTl\frac{\phi_2}{\phi_1} = RTl\frac{\pi_1}{\pi_2}, \qquad 229$$

where $\pi_1 > \pi_2$. When a change represented by 13 occurs in gases, we get mechanical energy; it does not seem possible to get electric energy. But when the change represented by 229 takes place in solutions, we may easily get electric energy. The conditions for the development of electric energy are easily obtained. A metal dipping into a solution of its salt admits of great variation in the concentration of its cations. Not that we can actually increase or decrease to any extent the number of gramcations in an aqueous solution without increasing at the same time the number of gramanions. We have seen that would produce very serious electric disturbances. But we may look upon the metal as a source of as many cations as we choose, or as a receptacle for the deposit of cations from solution; and a *slight change* in concentration of the cations we may suppose to take place, which slight change is shown by the potential.

Cations pass from the metal into the solution when the pressure of the cations from the metallic surface is greater than the osmotic pressure of the cations in the solution. When less than the osmotic pressure of the cations in the solution, cations deposit on the metal. In the first case the metal is left negatively charged, in the second case the metal is positively charged. In either case only a trace of ions can pass one way or the other. For the — charge produced on the

metal soon prevents further loss of + electricity on the part of the metal, and the excess of + electricity brought into the solution prevents increase of the electricity there. The + charge on the metal in the second case soon prevents further accumulation of cations on it, and the — electricity left in the solution soon prevents further loss of + electricity there. So a metal in a solution, if one of its salts does not produce a continuous current of electricity. An additional arrangement is needed whereby the charge on metal and in solution can be removed so fast as it is produced. When this is done, we have the conditions for the continuous development of electric energy.

104. **Potential difference and ionic tension.** — The maximum tension of the ions on the surface of a solid, we shall call the *ionic tension* of the solid. Assuming that the osmotic energy furnishes the electric energy, it is an easy matter to compute what the ionic tension of a metal must be in a combination M | MR solution to yield the observed electric energy. Since we agree always to refer to gramions, the capacity factor of the electric energy ϵ_0 is fixed, and we need only determine V to know the electric energy.

The electric energy of a gramcation is $= V\epsilon_0\eta$, where $\eta =$ valency of cation. The available volume energy of a gramcation in solution is $RTl\frac{\pi_0}{\pi}$, where π_0 is the ionic tension of the cation, and π the osmotic pressure of the cations in the solution. We shall suppose the solution normal, so

$$V\epsilon_0\eta = RTl\frac{\pi_0}{\pi},$$

or

$$V = \frac{RT}{\epsilon_0\eta} l\frac{\pi_0}{\pi}. \qquad 230$$

Hence

$$l\pi_0 = l\pi + \frac{V\epsilon_0\eta}{RT}0.4343, \qquad 231$$

where 0.4343 is the modulus of the Briggs system.

$$V\epsilon_0 = 96537 \cdot 10^7 \text{ ergs},$$

$$R = 2 \cdot 42750 \cdot 981 \text{ ergs},$$

$$\pi = 22 \cdot 76 \cdot 13.6 \cdot 981 \text{ dynes},$$

when we suppose the salt completely ionized; so at 25°,

$$l\pi_0 = 7.35 + \pi\eta \cdot 17.58. \qquad 232$$

Example. — For magnesium in a normal solution of a magnesium salt, supposing it completely ionized, at 25°,

$$V = 1.22,$$

and so $$l\pi_0 = 50.26,$$

or $$\pi_0 = 10^{50} \text{ dynes};$$

in atmospheres of 76 cm. Hg each,

$$\pi_0 = 10^{44} \text{ atmos.}$$

That is, assuming that the electric energy comes from the volume energy of the cations; to get the proper quantity of electric energy, the cations must have an initial pressure of 10^{44} atmos. It is enormous; but this is not a fatal objection, though it is a serious one, for we find no other indication of such enormous forces in metals.

Problems.

1. $Zn \mid ZnCl_2$ normal $= +0.51$ *V*. What is π_0? Aqueous solution. *Ans.* $\pi_0 = 10^{25}$ dynes $= 10^{19}$ atmos.

2. $Fe \mid FeCl_2$ normal $= +0.06$ *V*. What is π_0? Aqueous solution. *Ans.* $\pi_0 = 10^{9}$ dynes $= 10^{3}$ atmos.

3. $Cu \mid CuSO_4$ normal $= -0.66$ *V*. What is π_0? Aqueous solution. *Ans.* $\pi_0 = 10^{-14}$ dynes $= 10^{-20}$ atmos.

4. $Hg \mid HgNO_3$ normal $= -0.99$ *V*. What is π_0? Aqueous solution. *Ans.* $\pi_0 = 10^{-10}$ dynes $= 10^{-16}$ atmos.

5. $Ag \mid AgNO_3$ normal $= -1.01$ *V*. What is π_0? Aqueous solution. *Ans.* $\pi_0 = 10^{-10}$ dynes $= 10^{-20}$ atmos.

We see that the ionic tension of some metals is very great, of others, it is extremely small, while of others, like iron, it is quite moderate. We have in these figures a simple explanation of the sign of the charge on the metal in a solution of its salt. For when the ionic tension of the metal is greater than the osmotic pressure of its ions, cations pass into the solution, leaving the metal — charged, while when the ionic tension of the metal is very slight, cations deposit from the solution, charging the metal with + electricity.

From 230, when $\pi = 0$, that is, when there are no cations in the solution, $V = \infty$. As neither this value nor any approaching it has ever been observed, we are led to the conclusion that the instant a metal comes in contact with a liquid not containing ions of that particular metal, cations pass faster than we can follow from that metal into the liquid until there is a certain relation between the two pressures, which relation is given by the p.d.

Cations not composed of the particular metal considered are not supposed to affect the ionic tension of that metal. This idea comes from Dalton's law of partial pressures for gases. It hardly seems right to apply this law to solutions at such high osmotic pressures as we generally meet in solutions.

There is every reason to think that electrodes producing anions only would follow the same laws that metallic electrodes do. As yet we have not been able to get such electrodes, the nearest approach being a compound electrode such as AgCl, Hg with a layer of HgCl, etc., and gas electrodes (see § 106).

A cell of the type Hg, HgCl | H_2O, which is essentially Hg, HgCl | HgCl solution, for HgCl is somewhat soluble in water, is treated in the ordinary way, but a cell of the type Hg, HgCl | KCl solution cannot be so treated, for, on account of the $\bar{Cl}$ in the KCl solution, the $\dot{Hg}$ in solution is considerably diminished. We have studied this effect in § 69.

Let π_1 = the osmotic pressure of $\dot{Hg}$, and π_2 = the osmotic

pressure of $\bar{Cl}$. When pure H_2O is the solvent, $\pi_1 = \pi_2$, and $\pi_1\pi_2 = K$. When KCl is in solution, let π_2' = the osmotic pressure of the added $\bar{Cl}$ from the KCl, and π_1' = the new osmotic pressure of $\overset{+}{Hg}$. Then, since the osmotic pressure of $\bar{Cl}$ from HgCl is always = osmotic pressure of $\overset{+}{Hg} = \pi_1'$, we have,

$$\pi_1'(\pi_1' + \pi_2') = K,$$

or
$$\pi_1' = \tfrac{1}{2}(\sqrt{4K + (\pi_2')^2} - \pi_2'). \qquad 233$$

Substituting this value of π_1' for π in 230, gives

$$V = \frac{RT}{\epsilon_0 \eta}[l\pi_0 - l\tfrac{1}{2}(\sqrt{4K + (\pi_2')^2} - \pi_2')]. \qquad 234$$

In connection with 230, this equation will give us the solubility of very slightly soluble salts.

We see from 230 that the greater the concentration of the cations, other things being equal, the smaller the p.d. between metal and solution. In double cyanids of alkalies with heavy metals, the concentration of the heavy metal ion in aqueous solution is very slight. For instance, in a solution of $KAg(CN)_2$, the ions are $\overset{+}{K}$, $Ag(\bar{CN})_2$, $\overset{+}{K}$, $\overset{+}{Ag}$, $2\,\bar{CN}$. The concentration of $\overset{+}{Ag}$ is extremely slight.

Problems.

1. $Ag\,|\,KCN\ \frac{1}{10}$ normal $+ AgNO_3\ \frac{1}{100}$ normal $|\,KCl\,|\,AgNO_3\ \frac{1}{10}$ normal $|\,Ag = 1.14\ V$. What is the osmotic pressure of $\overset{+}{Ag}$ in the cyanid solution? Aqueous solutions? No p.d. between liquids. $T = 289$.

Ans. Osmotic pressure of $\overset{+}{Ag} = 10^{-13}$ dynes $= 10^{-20}$ atmos.

2. One liter of $KCN + AgNO_3$ normal solution has how much $\overset{+}{Ag}$.? KCN is in excess, as in problem 1.

Ans. $5 \cdot 10^{-20}$ grams $\overset{+}{Ag}$.

105. **Cells with active solutions.** — We have hitherto considered the electric energy due to the activity of the electrode. We shall now consider arrangements in which the electrode serves as a source of electricity for the ions and a deposit for the electricity from the ions. The electrodes do not react chemically, and therefore consist of some material like platinum, coke; in some special cases, especially as cathode, of copper, silver, etc.

Consider an arrangement

$$\mathrm{C} \mid \mathrm{A\ sol.} \mid \mathrm{B\ sol.} \mid \mathrm{C},$$

where C denotes an electrode of carbon, or any other inert substance, and A and B are two bodies which react chemically in such a way as to change the electric charges of the ions. Then the electricity needed for the change in the charges is taken from the electrodes.

For example:

$$\mathrm{C} \mid \mathrm{FeCl_2\ sol.} \mid \mathrm{Cl_2\ sol.} \mid \mathrm{C},$$

aqueous solution. $FeCl_2$ is ionized into $\overset{++}{\mathrm{Fe}} + 2\,\bar{\mathrm{Cl}}$; Cl_2 in aqueous solution is not ionized. But $\overset{++}{\mathrm{Fe}}$, in the presence of $3\,\bar{\mathrm{Cl}}$, readily changes into $\overset{+++}{\mathrm{Fe}}$; and Cl_2 under the corresponding conditions readily changes into $2\,\bar{\mathrm{Cl}}$. So in the cell, $3\,Cl_2$ becomes $6\,\bar{\mathrm{Cl}}$ and $6\,\overset{++}{\mathrm{Fe}}$ becomes $6\,\overset{+++}{\mathrm{Fe}}$, the $-$ electricity needed coming from the C on one side and the $+$ electricity needed coming from the C on the other side. So the electrode on the right side is charged with $+$ electricity and that on the left side with $-$ electricity.

In some such cases the reaction seems to proceed without any apparent electrode, the necessary electricity being taken from the containing vessel or from the solvent, or perhaps from the same source that the electricity for ionisation of MR comes from. For Au dissolves in Cl_2 water, giving $\overset{+++}{\mathrm{Au}} + 3\,\bar{\mathrm{Cl}}$, and must in some way get its needed charges of electricity.

The example of $FeCl_2$ and Cl_2 is very simple. A more complicated case would be

$$C \mid FeSO_4 \text{ sol.} \mid KMnO_4 + H_2SO_4 \text{ sol.} \mid C = 1.1\ V$$

in aqueous solution. Again, $\overset{++}{Fe}$ becomes $\overset{+++}{Fe}$. The other liquid changes thus:

$$2\ KMnO_4 + 3\ H_2SO_4 = K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + 5\ O,$$
$$5\ O + 5\ H_2SO_4 = 5\ H_2O + 5\ SO_4.$$

Each SO_4 takes $2-$ charges from the electrode on the right, leaving it $+$ charged. The rest of the matter is simple.

Very many other arrangements have been studied, but we need not consider them here, with one exception. An aqueous HCl solution of CuCl seems to dissolve both CO and O_2 from the air, provided the O_2 is immediately consumed, otherwise it reacts with CuCl. Therefore an arrangement

$$C,\ CO \mid CuCl \text{ sol.} \mid O_2,\ C$$

may be expected to yield electricity by the reaction

$$CO + O = \overset{++}{C}O + \overset{=}{O}.$$

When CO in contact with an inert electrode is passed into an aqueous HCl solution of CuCl, and O_2 in contact with another electrode is passed into the same solution, electric energy is produced; which energy amounts to more than the mechanical energy that would be obtained from the heat evolved on burning CO directly. It seems as if the electrode in contact with the O_2 has to be of Cu, and it may be that the electric energy comes chiefly from the reaction of this electrode with CuCl sol., and not from the O_2 and CO, so that the above explanation in this particular case may not be sufficient; but the direction of thought thereby illustrated has led to so many excellent agreements between theory and fact, that its general trend must be considered correct.

The ideal arrangement for getting electric energy seems to be

$$C \mid \text{some solution} \mid O_2, C,$$

which is intended to represent the oxidation of C by O_2. We cannot say that such an arrangement is possible, but there is no reason at present why we should not hope to realize it. But we cannot hope to do so until we learn more about the ionisation of CO_2 in solutions.

106. **Gas cells.** — The name is not very good, for gases do not seem to produce electricity directly. In reality gas cells are to be looked upon simply as cells in which gases are dissolved in inert electrodes, and are therefore to be treated like electrodes consisting of the gaseous bodies.

In Fig. 20, *A* is a tube containing a gas, *B* a tube containing the same gas under different pressure, or a different gas under any pressure. In each case the ionic tensions π_0 and π_0' are different. Through the top of each tube is sealed an electrode. The electrodes are partly in the gas, partly in a solution. The solution is, of course, in contact with the gases. In the reaction the ions get their charges from the electrodes, and pass into the solution. What is produced depends, of course, upon the gases. When one is H_2, and the other O_2, H_2O is produced; when one is H_2, the other Cl_2, HCl is produced; when one is H_2 under a certain pressure, and the other H_2 under a less pressure, $\overset{+}{H}$ passes

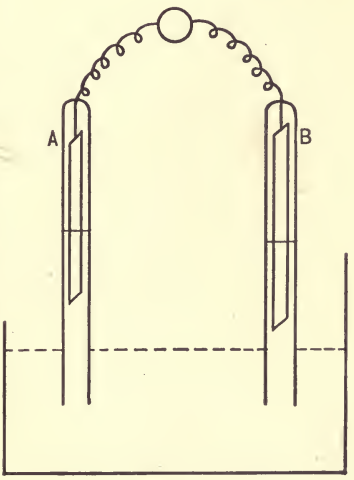

FIG. 20.

from the electrode with greater pressure, $\overset{+}{H}$ is deposited on the electrode with less pressure.

107. **Ionisation of water.** — Consider

$$H \mid KOH \text{ normal} \mid KCl \mid HCl \text{ normal} \mid H,$$

where H is the gas electrode, H in contact with an inert electrode, best Pd, and the solutions are aqueous. The pressure of the H_2 on the left and on the right are supposed alike. Hence π_0, the ionic tension of $\overset{+}{H}$, is the same on each side. On the left, the ionic pressure of $\overset{+}{H}$ is not counterbalanced by $\overset{+}{H}$ in solution to nearly so great an extent as on the right; on the contrary, $\overset{+}{H}$ on the left is immediately neutralized by $\overset{-}{OH}$ to form H_2O. So H_2 goes into solution as $2\overset{+}{H}$ on the left, and $2\overset{+}{H}$ passes into H_2 on the right. Let $\pi' =$ the osmotic pressure of $\overset{+}{H}$ in the KOH solution, which is very small, as H_2O is very slightly ionized, and this is diminished still more by the OH from the KOH; let $\pi'' =$ the osmotic pressure of $\overset{+}{H}$ in the HCl solution. Then for each electrode

$$V' = \frac{RT}{\epsilon_0 \eta} l \frac{\pi_0}{\pi'}, \quad \text{and} \quad V'' = \frac{RT}{\epsilon_0 \eta} l \frac{\pi_0}{\pi''}, \tag{235}$$

and the p.d. for the whole cell is

$$V = V' - V'' = \frac{RT}{\epsilon_0 \eta} l \frac{\pi''}{\pi'} = 0.6, \tag{236}$$

where the p.d. is counted from electrode to electrolyte.

Let c_1', $c_2' =$ the concentrations of the $\overset{+}{H}$ and $\overset{-}{OH}$ in the KOH solution, c_1'', $c_2'' =$ the same quantities in the HCl solution. Assume that KOH and HCl are completely ionized, then from the law of equilibrium,

$$c_1' c_2' = c_1'' c_2'' = K.$$

Hence

$$\frac{c_2'}{c_2''} = \frac{c_1''}{c_1'}. \tag{237}$$

Now $$\frac{c_1''}{c_1'} = \frac{\pi''}{\pi'},$$

and by condition $c_2' = c_1''$ for the ions from the water may be neglected as a sum or difference. Both c_2' and c_1'' are known, so all the quantities in 237 are to be considered known. Hence, if $c_1 = c_2$ are the concentrations of $\overset{+}{H}$ and $\overset{-}{OH}$ in water, we have

$$c_1 = c_2 = \sqrt{K} = \sqrt{c_1' c_2'} = \sqrt{c_1'' c_2''}.$$

PROBLEM.

Calculate the concentration of $\overset{+}{H}$ and $\overset{-}{OH}$ in 1000 cc. H_2O at 25°, assuming that KOH and HCl are completely ionized.

Ans. 10^{-5} gramions $\overset{+}{H}$ and $\overset{-}{OH}$.

108. **The chemometer.** — The chemometer is an instrument which measures the intensity of chemical activity just as the thermometer measures the intensity of heat activity, or the electrometer the intensity of electric activity. A body which has a higher mark than another body on the scale of the chemometer has a greater intensity of chemical activity than the second body.

By *chemical activity* of a body we mean the power of that body to react chemically. That is, when

$$A + BC = (1 - x)A + xAB + (1 - x)BC + xC,$$

and x is greater than $1 - x$, we say A has a greater chemical activity toward B than C has.

At one time the heat evolved was believed to measure the chemical activity of a body. So that if Q_1 was the heat liberated when a gramequivalent of A acted on C, and Q_2 was the heat liberated when a gramequivalent of B acted on C, and $Q_1 > Q_2$, then the chemical activity of A toward C was considered greater than the chemical activity of B toward C, — the

conditions, of course, being the same in each case; that is, the solutions are of equivalent concentrations, or if one body is precipitated and the other is not, correction is made for this. Of course no energy is supposed to escape in any form other than heat. From the second law of thermodynamics we learn that the availability of heat for mechanical work or any other energy is dependent upon the absolute temperature of the heat, and hence the quantity of heat evolved does not alone determine the available energy concerned in a chemical change. So to claim that chemical activity is measured by the heat of a reaction is very artificial from a theoretical side, let alone the fact that reactions do not always follow the line of greatest loss of heat.

We may say, however, in a general way, that a small quantity of heat, though at a high temperature, has less available energy than a large quantity of heat at a low temperature; and so it happens that a reaction producing a very large quantity of heat has more available energy than another reaction producing a very small quantity of heat, and is indeed a measure of the chemical activity, but a rough one, obviously not a scientific one.

Some chemists claim, however, that the available energy is no criterion of chemical activity; that the energy immediately produced in the chemical reaction is the true criterion. They forget, however, that when the conditions are proper, electric energy is as much an immediate product of chemical activity as heat energy is, if not more immediate.

Taking everything into consideration, it is pretty certain that electric energy is the true criterion of chemical activity. As the capacity is constant, $= \epsilon_0$, all we have to do is to measure the intensity V. How to measure V we have already considered. As the measurement is very simple with the capillary electrometer and the KCl | HgCl, Hg cell, it is a most valuable means whereby the chemist can determine the direction of a chemical reaction.

EXAMPLE. — $\text{Zn} \mid \overrightarrow{\text{ZnSO}_4 \text{ normal}} \mid \text{H, Pt} = 0.8\,V,$ *a*

$\text{Zn} \mid \overrightarrow{\text{ZnSO}_4 \text{ normal}} \mid \text{M}_1\text{SO}_4 \text{ normal} \mid \text{M}_1 = 0.9\,V,$ *b*

$\text{Zn} \mid \overrightarrow{\text{ZnSO}_4 \text{ normal}} \mid \text{M}_2\text{SO}_4 \text{ normal} \mid \text{M}_2 = 0.6\,V,$ *c*

where M_1, M_2 denote metals. Aqueous solutions. Since the p.d. of the second combination is greater than that of the first,

$$\text{p.d. of Pt, H} \mid \text{M}_1\text{SO}_4 \text{ normal} > \text{p.d. of M}_1 \mid \text{M}_1\text{SO}_4 \text{ normal},$$

so Pt, H decomposes a solution of M_1SO_4, depositing the M_1, H taking the electric charge from M_1. This is the case whenever a combination like *b* has a p.d. $> 0.8\,V$.

PROBLEMS.

1. When a combination like *c* has a p.d. $< 0.8\,V$, will Pt, H decompose a solution containing the metal, M_2? Why?

2. Pt seems to absorb H_2O_2 as it does H_2. Pt in neutral aqueous sol. H_2O_2 has p.d. $= -1.03\,V$ about, in an acidified aqueous sol. H_2O_2, the p.d. $= -1.08\,V$ about, in an alkalin aqueous sol. H_2O_2, p.d. $= -0.37\,V$ about. Explain this.

3. $$\text{Ag, AgBr} \mid \text{KBr} = -0.42\,V.$$

Will neutral, acid, or alkalin aqueous solutions of H_2O_2 decompose AgBr so that the solution of H_2O_2 can be used as a developer? Why?

4. There are two forms of HgO, red and yellow.

$$\text{Hg, } \underset{\text{red}}{\text{HgO}} \mid \text{KOH} \mid \underset{\text{yellow}}{\text{HgO}}\text{, Hg} = 0.000\,V.$$

What is the chemical difference between these two forms of HgO? Why?

109. **Potential difference between simple cells of different concentration.** — Consider the two cells

$$\text{Hg, HgCl} \mid \text{ZnCl}_2\ a \text{ normal} \mid \text{Zn}, \qquad (1)$$

$$\text{Hg, HgCl} \mid \text{ZnCl}_2\ b \text{ normal} \mid \text{Zn}, \qquad (2)$$

where $a > b$. Suppose Zn is connected to Zn and Hg to Hg. From the problems on page 188 we see that the ionic pressure of Zn is much greater than that of Hg, hence $\overset{++}{\text{Zn}}$ tends to pass into solution and not $\overset{+}{\text{Hg}}$, when each cell is considered separately. But considered together, in the second cell the osmotic pressure of $\overset{++}{\text{Zn}}$ in solution is less than in the first cell, and so $\overset{++}{\text{Zn}}$ passes into solution in the second cell a corresponding $2\,\overset{-}{\text{Cl}}$ from the HgCl meeting it. The + electricity thereupon set free from HgCl passes over to the first cell and meets with a corresponding $2\,\overset{-}{\text{Cl}}$ from the ZnCl_2 in solution, and the $\overset{++}{\text{Zn}}$ deposits its + electricity on the Zn electrode which there meets with the − electricity from the Zn electrode of the second cell.

Let π_1 be the osmotic pressure of $\overset{++}{\text{Zn}}$ in the first cell, π_2 that in the second cell, V_1 the p.d. in the first cell, V_2 that in the second cell. The concentration of $\overset{+}{\text{Hg}}$ being insignificant in each cell, the osmotic energy of $\overset{+}{\text{Hg}}$ may be considered insignificant in comparison with that of $\overset{++}{\text{Zn}}$.

Assume that the quantity of ZnCl_2 produced or lost is so small compared with the total quantity of ZnCl_2 in solution as not to make any appreciable difference in the concentration of the solution. When $\overset{++}{\text{Zn}}$ is produced or lost, $2\,\overset{-}{\text{Cl}}$ are likewise produced or lost, and so the osmotic energy corresponds to 3 gramions. Since $\eta = 2$, we have for the double cell

$$V = V_2 - V_1 = \frac{3}{2}\frac{RT}{\epsilon_0} l \frac{\pi_1}{\pi_2}.$$

For any cell of the above type,

$$V=\frac{n}{\eta}\cdot\frac{RT}{\epsilon_0}l\frac{\pi_1}{\pi_2}, \qquad 238$$

where n denotes the number of gramions produced in the solution when 1 gramion of the active metal is produced.

PROBLEM. — Suppose that for $ZnCl_2$, $x=\frac{2}{3}$, what would 238 become? Why? *Ans.* $V=\frac{1+2x}{2}\cdot\frac{RT}{\epsilon_0}l\frac{\pi_1}{\pi_2}$.

We notice that as V is independent of the metal of the insoluble salt, Hg may be replaced by Cu^I, Pb, Ag, etc., without changing the value of V. Also that when the relation between π_1 and π_2 is kept constant, various metals may be substituted for Zn without changing the value of V. Experiment has justified these conclusions.

110. **Potential difference between solutions.** — Consider the cell

$$\text{Zn}\,|\,ZnCl_2\ a\ \text{normal}\ \overleftarrow{|}\ ZnCl_2\ b\ \text{normal}\,|\,\text{Zn},$$

where $a>b$. Aqueous solutions. Assume the quantity of each solution is so great that no appreciable change in concentration is produced in the following operation. Since $a>b$, $\overset{++}{\text{Zn}}$ is formed from right electrode and deposited on left electrode. While the gramion is being produced, some $\overset{++}{\text{Zn}}$ migrates toward the cathode. This quantity is

$$\text{U}/(\text{U}+\text{V}) = \text{U}/\mu_\infty \text{ gramions},$$

so that the gain in concentration is not 1 gramion, but

$$(1-\text{U})/\mu_\infty = \text{V}/\mu_\infty \text{ gramions}.$$

At the cathode, on the other hand, the loss is only

$$(1-\text{U})/\mu_\infty = \text{V}/\mu_\infty.$$

Hence, assuming that $ZnCl_2$ is completely ionized,

$$V = \pi_2 - \pi_1 = \frac{3}{2}\frac{V}{\mu_\infty}\frac{RT}{\epsilon_0}\left[l\frac{\pi_0}{\pi_2} - l\frac{\pi_0}{\pi_1}\right] = \frac{3}{2}\frac{V}{\mu_\infty}\frac{RT}{\epsilon_0}l\frac{\pi_1}{\pi_2}. \qquad 239$$

PROBLEM.

Ag, AgCl | KCl a normal | KCl b normal | AgCl, Ag. Deduce the expression for V. Aqueous solutions.

Ans. $V = -\frac{U}{\mu_\infty}\frac{RT}{\epsilon_0}l\frac{\pi_1}{\pi_2}$.

Suppose Pt | KCl a normal | KCl b normal | Pt, where $a > b$, and solution so large in quantity that the concentration does not appreciably change during the operation. The electrodes are intended only to furnish electricity, not to take part in the operation.

Assume that ϵ_0 passes through the cell. The change in osmotic energy in the direction of the current and due to $\overset{+}{K}$ is

$$\frac{U}{\mu_\infty}nRTl\frac{\pi_1}{\pi_2},$$

where π_1, π_2 are the osmotic pressures of $\overset{+}{K}$ on the right side and left side respectively, and n the number of cations. The change in osmotic energy in the direction opposite to the current and due to $\overset{-}{Cl}$ is

$$\frac{V}{\mu_\infty}nRTl\frac{\pi_1}{\pi_2},$$

where n is now the number of anions. The difference between these quantities gives the osmotic energy available for electric energy, and so

$$V = \frac{U - V}{\mu_\infty}\frac{nRT}{\epsilon_0\eta}l\frac{\pi_1}{\pi_2}. \qquad 240$$

The direction of the current is such that the difference in concentration is equalized. So that, when the cation is the faster, the current passes from concentrated to dilute solution, from a to b; when the anion the faster, the current passes from dilute to concentrated solution, from b to a; when $U = V$, there is no current. In general, $U - V$ is small, and so V is usually small at the boundary of two solutions.

PROBLEMS.

1. $$Pt \mid HCl \text{ normal} \mid H_2O \mid Pt.$$

Neglecting $Pt \mid HCl$ normal and $Pt \mid H_2O$; $U = 325$, $V = 70$. Neglecting ionisation of H_2O, in what direction does the current pass? Why? Aqueous solutions.

2. $$Pt \mid KOH \text{ normal} \mid H_2O \mid Pt.$$

Neglecting $Pt \mid KOH$; $U = 71$, $V = 170$; otherwise as in No. 1. In what direction does the current pass? Why?

The principle of equalization of differences, which principle seems to run through all natural phenomena, can be applied to the other concentration cells.

In the system,

$$Hg, HgCl \mid ZnCl_2\ a \text{ normal} \mid Zn, \qquad 1$$

$$Hg, HgCl \mid ZnCl_2\ b \text{ normal} \mid Zn, \qquad 2$$

where $a > b$, the only action possible that equalizes the concentrations is that whereby Zn dissolves in 2 and separates in 1. The energy available for electric energy is the change in osmotic energy thereby produced.

In the system,

$$Zn \mid ZnCl_2\ a \text{ normal} \mid ZnCl_2\ b \text{ normal} \mid Zn,$$

where $a > b$, the only action possible that equalizes the concentrations is that whereby Zn dissolves on the right and

separates on the left. The energy available for electric energy is the change in osmotic energy.

This principle avoids the necessity of assuming an ionic tension in these cells. Possibly it will let us do away with the ionic tension in all cells, but that can only come later. As yet we need the ionic tension idea in the other cells.

111. **Polarization.** — Consider a cell of the type

$$M \mid \overrightarrow{HCl}, \text{ aqueous sol.} \mid M_1,$$

where M and M_1 are inert electrodes, and suppose a slight p.d. in the direction of the arrow. $\overset{-}{Cl}$ deposits on M, and $\overset{+}{H}$ on M_1. The result is that M becomes an electrode of Cl, and M_1 becomes an electrode of H. But Cl and H each have an ionic tension, and so a p.d. is set up in a direction opposite to the initial current. The electrodes change their nature, and then the cell is said to be polarized. A polarized cell is a cell in which a p.d. opposite to the initial p.d. is set up.

We started with a very weak p.d., so that the p.d. due to polarization more or less completely neutralizes this, reducing the initial or primary p.d. nearly or quite to zero. The polarizing p.d. difference cannot of course rise above the initial or primary p.d. As the primary p.d. is increased, the polarizing p.d. rises to meet it, until a certain value is reached, above which the polarizing p.d. does not follow. For every combination of bodies there is a certain maximum p.d., and when the electrodes are completely covered by any two bodies, the p.d. then reaches its maximum value. The polarizing bodies then commence to give off their electricity and to become neutral, passing off as gases, or precipitating as coatings or as flakes, provided the primary p.d. is above the maximum polarizing p.d. In the supposed example H_2 and Cl_2 are freely evolved. Until the maximum value is reached the ions retain their electricity, refusing to appear as ordinary bodies. This is explained by saying that a certain p.d. is needed before we

can cause an ion to give up its electricity and become neutral. We shall call this the electric tenacity of the ion. Different ions have different electric tenacity, and therefore metals can be separated quantitatively by electricity.

When the cathode is polarized, we call it cathodic polarization; anodic polarization is the polarization of the anode.

PROBLEM. — Write down a cell showing anodic polarization.

Cells that polarize are called inconstant cells because the p.d. between the electrodes drops so soon as the cell commences to act; cells that do not polarize have a constant p.d. difference, and are called constant cells.

112. **Constant cells.** — Cells that are used to produce electricity are always constant cells. Constant cells can always be obtained by having each electrode dip into a solution of one of its salts, usually an aqueous solution, or by covering the electrode with an insoluble salt.

For instance,

$Zn \mid ZnSO_4$ sol. $\mid CuSO_4$ sol. $\mid Cu = 1.10$ about. Daniell cell.

$Zn \mid ZnCl_2$ sol. $\mid HgCl, Hg = 1.1\ V$ about. Calomel or Helmholtz cell.

$Zn \mid ZnSO_4$ sol. $\mid HgSO_4, Hg = 1.43\ V$ about. Clark cell.

Substances that prevent polarization are called depolarizers.

PROBLEM. — What are the depolarizers in the above examples? Why?

Constant cells can often be obtained by using something that will remove the substance that would otherwise deposit on the electrode.

For instance,

$$Zn \mid H_2SO_4 \text{ sol.} \mid HNO_3 \mid C \text{ or } Pt = 1.9\ V \text{ about.}$$

$$Zn \mid H_2SO_4 \text{ sol.} \mid H_2CrO_4 \text{ sol.} \mid C = 2.0\ V \text{ about.}$$

PROBLEM. — What are the depolarizers here? Why?

Cells of the type considered in § 105, in which the electrodes do not receive any deposit nor give up matter to the reaction, the electrodes only serving to furnish electricity for the ions, are also constant so long as the concentrations of the solutions do not change.

113. **Electrolytic separations.** — Suppose we have an aqueous solution containing $Cu(NO_3)_2$, $AgNO_3$, $Mn(NO_3)_2$, $HgNO_3$, $Ca(NO_3)_2$, $NaNO_3$, and we pass a current of electricity through it, using Pt electrodes. Let us commence with a very small p.d. This produces a polarization only, but on gradually increasing the p.d. a value is finally reached at which a metal separates. The separation is dependent upon two things, the electric tenacity of each metal, and the concentration of its ions compared with the quantity of electricity on the cathode. So long as the ions of the metal are present in quantity, that metal separates first which has the smallest electric tenacity, but by degrees the ions of this metal are reduced to such a small amount that the p.d. at the cathode can rise to that value at which another metallic ion gives up its electricity and begins to separate. However, by carefully regulating the flow of electricity, the p.d. at the cathode can be kept at such a value that when the second metal begins to separate, the first one has separated so completely that chemical analysis is unable to show its presence in the solution.

The electric tenacities are in the same order as the polarization values. So the metal which first separates is the one having the smallest p.d. against the solution.

As we increase the p.d. at the cathode, removing each metal as it separates until we come to Ca, we do not get this metal, but H_2 instead. Though $\overset{+}{H}$ is present in but very small quantity in aqueous solutions of metallic salts, yet the electric tenacity of $\overset{+}{Ca}$ is so much greater than that of $\overset{+}{H}$ that the latter separates first. When we make it more difficult for $\overset{+}{H}$ to change to H_2, by using surfaces which seem to prevent inti-

mate contact with $\overset{+}{H}$, such as a mercury surface, then we find it possible to separate quantitatively some metals which could not otherwise be separated quantitatively. So mercury makes a very useful electrode in quantitative electrolytic separations. Even then, however, Ca cannot be separated quantitatively, only qualitatively. Only those metals can be separated quantitatively with a mercury electrode which have a p.d. against the solution not much greater than $\overset{+}{H}$ has on electrodes of ordinary surface.

114. **Electrochemical analysis.** — Consider a cell of the type

$$M \mid MR \text{ sol.} \mid MR \text{ sol.} \mid M,$$

in which M is the same throughout, and the solutions are of equal concentrations. The p.d. is of course zero. Now suppose we add to one of the solutions a soluble salt M_1R_1 which reacts with M to form an insoluble salt MR_1. As M gradually precipitates from say the left-hand solution, the p.d. rises, and just when all M has combined to form the insoluble salt, the p.d. suddenly leaps up. The salt MR which remains in the solution does not interfere. In this way solutions can be analyzed volumetrically with great precision.

Similarly the combination

$$M \mid M_1R_1 \text{ sol.} \mid MR \text{ sol.} \mid M$$

can be used. In this case MR is added, and MR_1 is insoluble; so the p.d. is high at first and gradually diminishes until, just when all R_1 has precipitated, it drops rapidly.

Salts which do not precipitate MR do not interfere, provided the electrode M does not decompose them.

PROBLEM.

The cell is

$$Ag \mid AgNO_3 \; a \text{ normal} \mid AgNO_3 \; a \text{ normal} \mid Ag.$$

The solution on the left side measures 8.02 cc. The first column gives number of cc. of $\frac{1}{10}$ normal KCl added; the second column, the p.d. in volts.

cc.	V	cc.	V
7.87	0.102	8.02	0.132
7.93	0.108	8.05	0.186
7.97	0.114	8.07	0.240

The cell is

$$\text{Hg} \mid \text{KBr } a \text{ normal} \mid \text{HgNO}_3 \ a \text{ normal} \mid \text{Hg},$$

the solutions being kept separated by an intermediate solution of KNO_3 or some other harmless salt. The precipitating solution is of course $HgNO_3$ $\frac{1}{10}$ normal. The solution on the left side measures 10 cc.

cc.	V	cc.	V
0.00	0.466	9.94	0.359
5.00	0.457	9.99	0.320
7.49	0.448	10.04	0.080
8.49	0.432	10.11	0.060
9.49	0.401	10.99	0.031
9.79	0.382	12.99	0.022
9.89	0.367		

What is the composition of the $AgNO_3$ solution and the KBr solution?

115. **Accumulators.** — An accumulator is a cell which absorbs relatively large quantities of electricity under certain conditions, and gives off this electricity readily and without substantial injury when the conditions are changed. When it has absorbed the proper quantity of electricity, the accumulator is said to be charged. When it has lost its electricity, it is said to be discharged. Charging and discharging accumulators gradually destroys them, but a good accumulator stands a great many charges and discharges.

Consider a cell of the type

$$\overrightarrow{\text{M}_1 \mid \text{M}_1\text{R sol.} \mid \text{M}_2\text{R sol.} \mid \text{M}_2},$$

and pass a current through in a direction opposite to the arrow, so that we have

$$M_1 \,|\, M_1R \text{ sol.} \overleftarrow{|} M_2R \text{ sol.} \,|\, M_2.$$

M_1R and M_2R are in aqueous solution and prevented from mixing so far as possible by using porous cups or by gravity.

After a sufficient quantity of electricity has been absorbed by the cell, disconnect from the external source of electricity. Then on connecting the electrodes we get a flow of electricity in the direction of the arrow in the first case. After the quantity of electricity put in has come out, the cell does not stop producing it, but electricity flows until one of the constituents is consumed or until the solutions have mixed. In so far as the cell absorbs electricity, the cell just considered is an accumulator. In practice, however, such cells are not used. The solutions cannot be prevented from ultimately mixing, and unless carefully watched there is danger of completely dissolving one of the electrodes with disastrous results when the cell is doing important work.

The cell commonly used as an accumulator is of the form when charged,

$$PbO_2 \,|\, H_2SO_4 \text{ 20\% aqueous sol.} \,|\, Pb.$$

In discharging,

$$PbO_2 + 2\overset{+}{H} + 2\overset{+}{H} + \overset{=}{SO}_4 = PbSO_4 + 2\,H_2O,$$

so that the PbO_2 electrode becomes + and changes to $PbSO_4$ as the accumulator is discharged.

The other electrode reacts, thus

$$Pb + 2\overset{+}{H} + \overset{=}{SO}_4 = PbSO_4 + 2\overset{+}{H},$$

which $2\overset{+}{H}$ is used in the preceding reaction. So that this electrode becomes — and changes into $PbSO_4$ as the accumulator is discharged. On charging, the reverse changes take place. These equations are only intended to give a general idea; *just* what happens, no one knows.

CHAPTER X.

IONS.

116. **Some general properties of the ions.** — In these last pages we consider some properties of the ions which do not seem to fit in elsewhere. Again the student is reminded that the existence of ions is entirely hypothetical, and we may at any time find it necessary to replace the ionic theory by another one.

Ions are formed most readily in the liquid state, either in a melted solid or in a solution. Some solids, however, conduct electrolytically and are therefore supposed to contain ions. Some melted solids do not conduct electrolytically, and so such do not contain ions, at least not more than traces. Some solutions do not conduct electrolytically, so such solutions do not contain ions. We have not yet discovered a general regulating law in regard to the formation of ions; nothing more than empirical rules.

The solvent has much to do with ionic state. We have considered in what way. Water is the solvent most favorable to ionisation of solutes, but water itself is but slightly ionized. There is no explanation of this.

117. **Heat of ionisation.** — When a dilute aqueous solution of a monovalent acid and a monovalent base are mixed, we have the reaction,

$$\overset{+}{H} + \overset{-}{R} + \overset{+}{M} + \overset{-}{OH} = \overset{+}{M} + \overset{-}{R} + H_2O + Q,$$

the water as solvent not taking part. So the only reaction is that of $\overset{+}{H}$ and $\overset{-}{OH}$ to form H_2O. We claim that these combine because water is so slightly ionized. Hence Q is really the

heat of ionisation of water. So solutions of completely ionized acids and bases, of equivalent strength, should have the same heats of neutralization. This seems to be the case, and the heat of neutralization is $Q = -13500$ cals., so

$$\overset{+}{H} + \overset{-}{OH} = H_2O - 13500 \text{ cals.},$$

meaning that 13500 cals. are given off.

With this value as a basis, we can determine the heats of ionisation of many salts in aqueous solutions.

Suppose we treat 1 grammolecule of a *weak* monovalent acid with 1 grammolecule of NaOH in dilute solution, both aqueous; we have

$$(1-x)HR + x\overset{+}{H} + x\overset{-}{R} + \overset{+}{Na} + \overset{-}{OH} = \overset{+}{Na} + \overset{-}{R} + H_2O + Q, \qquad 241$$

where Q is the heat of the reaction. But obviously

$$Q_1(1-x) = 13500 - Q, \qquad 242$$

where Q_1 is the heat of ionisation of HR. The degree of ionisation of $HR = x$ can be found by one of the numerous ways, and as Q is given by the experiment, Q_1 can be computed by 242.

When the base is not completely ionized, nor the salt either,

$$(1-x)HR + x\overset{+}{H} + x\overset{-}{R} + (1-y)MOH + y\overset{+}{M} + y\overset{-}{OH}$$
$$= z\overset{+}{M} + z\overset{-}{R} + (1-z)MR + H_2O - Q. \qquad 243$$

Whence $Q_1(1-x) + Q_2(1-y) + Q_3(1-z) = 13500 - Q, \qquad 244$

which requires two more determinations under such conditions that two of the quantities, x, y, z, separately vanish before we can get Q_1, Q_2, Q_3.

Problem. — What are these conditions?

118. **Formation of ions.** — Ions are formed in the following ways:

(1) A neutral body divides into cations and anions;

$$MR = \overset{+}{M} + \overset{-}{R}.$$

(2) A neutral body takes a charge originally on an ion, which thereupon becomes neutral;

$$\overset{+}{M}_1 + \overset{-}{R} + M_2 = \overset{+}{M}_2 + \overset{-}{R} + M_1.$$

(3) A neutral body becomes a cation while another neutral body becomes an anion;

$$2\,M + Cl_2 = 2\,\overset{+}{M} + 2\,\overset{-}{Cl}.$$

(4) Ions increase in valency;

$$2\,\overset{++}{Fe} + 4\,\overset{-}{Cl} + Cl_2 = 2\,\overset{+++}{Fe} + 6\,\overset{-}{Cl}.$$

In general those reactions whereby the quantities of electricity on the right side and on the left side of the reaction are made unequal are available for producing electricity.

APPENDIX.

APPENDIX.

TABLE I.

LOGARITHMS. Proportional Parts.

Nat. numb.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0212	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	11	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

TABLE I. — *Continued.*

Nat. numb.	LOGARITHMS. 0	1	2	3	4	5	6	7	8	9	Proportional Parts. 1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7704	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

TABLE II.

Volume and density of water at different temperatures (ROSSETTI).

Temp. ° C.	Volume of Water (at 0° = 1).	Sp. Gr. of Water (at 0° = 1).	Volume of Water (at 4° = 1).	Sp. Gr. of Water (at 4° = 1).
0	1.00000	1.000000	1.00013	0.999871
1	0.99994	1.000057	1.00007	0.999928
2	0.99990	1.000098	1.00003	0.999969
3	0.99988	1.000120	1.00001	0.999991
4	0.99987	1.000129	1.00000	1.000000
5	0.99988	1.000119	1.00001	0.999990
6	0.99990	1.000099	1.00003	0.999970
7	0.99994	1.000062	1.00007	0.999933
8	0.99999	1.000015	1.00011	0.999886
9	1.00005	0.999953	1.00018	0.999824
10	1.00012	0.999876	1.00025	0.999747
11	1.00022	0.999784	1.00034	0.999655
12	1.00032	0.999678	1.00045	0.999549
13	1.00044	0.999559	1.00057	0.999430
14	1.00057	0.999429	1.00070	0.999299
15	1.00071	0.999289	1.00084	0.999160
16	1.00087	0.999131	1.00100	0.999002
17	1.00103	0.998970	1.00116	0.998841
18	1.00122	0.998782	1.00135	0.998654
19	1.00141	0.998588	1.00154	0.998460
20	1.00161	0.998388	1.00174	0.998259
21	1.00183	0.998176	1.00196	0.998047
22	1.00205	0.997956	1.00217	0.997828
23	1.00228	0.997730	1.00240	0.997601
24	1.00251	0.997495	1.00264	0.997367
25	1.00276	0.997249	1.00289	0.997120
26	1.00301	0.996994	1.00314	0.996866
27	1.00328	0.996732	1.00341	0.996603
28	1.00355	0.996460	1.00368	0.996331
29	1.00383	0.996179	1.00396	0.996051
30	1.00412	0.99589	1.00425	0.99577
40	1.00757	..	..	..
50	1.01182	..	..	..
60	1.01678	..	..	..
70	1.02243	..	..	..
80	1.02874	..	..	..
90	1.03554	..	..	..
100	1.04299	..	..	..

TABLE III.

Pressure (tension) of water vapor between −19° and 101° C. (BROCH).

T. ° C.	mm.	T. ° C.	mm.	T. ° C.	mm.	T. ° C.	mm.
−19	1.0288	12	10.4322	43	64.3104	74	276.8675
−18	1.1202	13	11.1370	44	67.7568	75	288.7640
−17	1.2187	14	11.8835	45	71.3619	76	301.0860
−16	1.3248	15	12.6739	46	75.1314	77	313.8475
−15	1.4390	16	13.5103	47	79.0714	78	327.0549
−14	1.5618	17	14.3950	48	83.1883	79	340.7265
−13	1.6939	18	15.3304	49	87.4882	80	354.8730
−12	1.8357	19	16.3189	50	91.9780	81	369.5075
−11	1.9880	20	17.3632	51	96.6644	82	384.6432
−10	2.1514	21	18.4659	52	101.5541	83	400.2933
−9	2.3266	22	19.6297	53	106.6546	84	416.4721
−8	2.5143	23	20.8576	54	111.9730	85	433.1938
−7	2.7153	24	22.1524	55	117.5162	86	450.4730
−6	2.9304	25	23.5174	56	123.2925	87	468.3240
−5	3.1605	26	24.9556	57	129.3095	88	486.7635
−4	3.4065	27	26.4705	58	135.5750	89	505.8059
−3	3.6693	28	28.0654	59	142.0973	90	525.4676
−2	3.9499	29	29.7439	60	148.8848	91	545.7650
−1	4.2493	30	31.5096	61	155.9456	92	566.7149
0	4.5687	31	33.3664	62	163.2889	93	588.3349
+1	4.9091	32	35.3181	63	170.9236	94	610.6426
2	5.2719	33	37.3689	64	178.8585	95	633.6567
3	5.6582	34	39.5228	65	187.1028	96	657.3956
4	6.0693	35	41.7842	66	195.6663	97	681.8791
5	6.5067	36	44.1577	67	204.5586	98	707.1271
6	6.9718	37	46.6477	68	213.7895	99	733.1602
7	7.4660	38	49.2950	69	223.3691	100	760.0000
8	7.9909	39	51.9965	70	233.3079	101	787.6678
9	8.5484	40	54.8651	71	243.6163		
10	9.1398	41	57.8700	72	254.3048		
11	9.7671	42	61.0167	73	265.3849		

Table IV.

Density of saturated water vapor and corresponding pressure at different temperatures. Density in grams per liter; pressure in mm. Hg.

t.	p.	d.	t.	p.	d.
0°	4.60	0.0047	110°	1075.4	0.8401
10°	9.16	0.0092	120°	1491.3	1.1426
20°	17.39	0.0170	130°	2030.3	1.5272
30°	31.55	0.0301	140°	2717.6	2.0092
40°	54.91	0.0509	150°	3581.2	2.6048
50°	91.98	0.0830	160°	4651.6	3.3322
60°	148.79	0.1307	170°	5961.7	4.2105
70°	233.08	0.1994	180°	7546.4	5.2604
80°	354.62	0.2959	190°	9442.7	6.5019
90°	525.39	0.4284	200°	11689.0	7.9554
100°	760.00	0.6062			

Table V.

Specific heats between 15° and 100°.

Lead	0.032	Copper . . .	0.094	Silver	0.057
Iron	0.113	Brass	0.094	Zinc	0.094
Glass	0.190	Nickel . . .	0.110	Tin	0.056
Gold	0.032	Platinum . .	0.032	Mercury . . .	0.034

Table VI.

Heats of vaporization q', and of fusion q'', in cals.

	q'.	q''.		q'.	q''.
Ether	90	30	Toluene	..	85
Ethyl acetate . . .	90	..	Water	536	..
Ethyl bromide . .	60	..	Xylene	..	39
Ethyl alcohol . . .	210	..	Lead	..	6
Anilin	93	..	Platinum	..	27
Benzene	94	..	Mercury	62	28
Chloroform . . .	58	..	Sulfur	362	9
Acetic acid . . .	97	46	Silver	..	21
Methyl alcohol . .	266	..	Zinc	..	28
Naphthalene . . .	..	36	Tin	..	13
Phenol	..	25	KNO_3	..	49
Carbon disulfid . .	90	..	$NaNO_3$	...	65

TABLE VII.

Electric conductivity of metals at 18° in mhos.

Antimony . . . 2.2	German silver, 2.5 to 6.4	Nickelin . 2.4
Bismuth 0.85	Gold . . . . . 43.	Platinum . 6.9
Brass . . 11.7 to 14.8	Iron . . . 7.4 to 9.5	Silver . . 63.
Carbon (gas coke), 0.02	Lead 4.8	Tin . . . 8.5
Copper . . . . 58.	Mercury 1.044	Zinc . . 16.

TABLE VIII.

Electric conductivity in Hg units of aqueous solutions of salts and acids at 18°. The figures give per cent of salt in 100 parts of solution. Salts are anhydrous. Δc denotes increase of conductivity for 1° in per cent of c.

Solution.	NaCl		NH_4Cl		Na_2SO_4		$MgSO_4$		$CuSO_4$	
	10^7c	Δc	10^7c	Δc	10^7c	Δc	10^7c	Δc	10^7c	Δc
5%	63	2.2	86	2.0	38	2.4	24	2.3	18	2.2
10	113	2.1	166	1.9	64	2.5	39	2.4	30	2.2
15	153	2.1	242	1.7	83	2.6	45	2.5	39	2.3
20	183	2.2	315	1.6			45	2.7		
25	200	2.3	376	1.5			39	2.9		

Solution.	NHO_3		HCl		H_2SO_4		KJ		$ZnSO_4$		$AgNO_3$		KOH	
	10^7c	Δc	10^7c	Δc	10^7c	Δc	10^7c	Δc	10^7c	Δc	10^7c	Δc	10^7c	Δc
5%	241	1.50	369	1.59	195	1.21	32	2.1	18	2.3	24	2.2	161	1.9
10	431	1.45	590	1.57	366	1.28	64	2.0	30	2.3	44	2.2	295	1.9
15	573	1.40	698	1.56	508	1.36	98	1.9	39	2.3	64	2.2	399	1.9
20	665	1.38	713	1.55	611	1.45	136	1.8	43	2.4	81	2.1	468	2.0
25	720	1.38	677	1.54	671	1.54	175	1.8	44	2.6	99	2.1	506	2.1
30	734	1.39	620	1.53	691	1.62	215	1.7	41	3.0	116	2.1	508	2.3
35	719	1.43	553	1.52	678	1.70	257	1.6	33	4.0	131	2.1	477	2.4
40	686	1.49	483		636	1.78	296	1.5			146	2.1	422	2.7
50	590	1.6			505	1.93	367	1.4			173	2.1		
60	480	1.6			349	2.13	416	1.4			196	2.1		
70	370	1.5			202	2.56								
80	250	1.3			103	3.49								

Table VIII. — *Continued.*

The solutions have maximum conductivity.

HNO_3	$c\,10^7 = 734$	at	29.7 %
HCl	717		18.3
H_2SO_4	691		30.4
KOH	510		28
$MgSO_4$	46.1		17
$ZnSO_4$	44.2		23.5

Table IX.

Migration values of the *anions* v, in gramequivalent solutions at 18°.

KOH	0.74	NaCl	0.63	$\frac{1}{2}\,CaCl_2$	0.69
KCl	0.51	$NaNO_3$	0.61	$\frac{1}{2}\,MgCl_2$	0.71
KBr	0.52	$NaC_2H_3O_2$	0.42	$\frac{1}{2}\,MgSO_4$	0.66
KI	0.51	$\frac{1}{2}\,Na_2SO_4$	0.64	$\frac{1}{2}\,ZnCl_2$	(0.7)
KNO_3	0.49	$\frac{1}{2}\,Na_2CO_3$	0.55	$\frac{1}{2}\,ZnSO_4$	0.68
$KC_2H_3O_2$	0.33	LiOH	0.88	$\frac{1}{2}\,CuSO_4$	0.70
$\frac{1}{2}\,K_2SO_4$	0.50	LiCl	0.74	$AgNO_3$	0.50
$\frac{1}{2}\,K_2CO_3$	0.43	$\frac{1}{2}\,Li_2SO_4$	(0.7)	HCl	0.17
NH_4Cl	0.51	$\frac{1}{2}\,BaCl_2$	0.64	HNO_3	0.17
NaOH	0.83	$\frac{1}{2}\,SrCl_2$	0.65	$\frac{1}{2}\,H_2SO_4$	0.17

Table X.

Relative velocities of the ions, U and V, at 18°.

H	300	$\frac{1}{2}\,Sr$	(50)	Br	62
K	60	$\frac{1}{2}\,Ca$	(46)	I	62
Na	41	$\frac{1}{2}\,Mg$	(46)	NO_3	58
Li	33	$\frac{1}{2}\,Zn$	(46)	ClO_3	52
NH_4	60	$\frac{1}{2}\,Cu$	(48)	HCOO	44
Ag	52	OH	165	CH_3COO	33
$\frac{1}{2}\,Ba$	(52)	Cl	63	$\frac{1}{2}\,SO_4$	(66)

Table XI.

Constants of ionisation, K, and solubility, s, of some carbon acids. Solubility expressed in grams per 1000 cc. solution. Degree of ionisation, $x = \mu_v/\mu_\infty$, where μ_v is the molecular conductivity at concentration given by s.

Acid.	K.	s.	x.
Anisic	0.0_432	0.2263	0.1363
Benzoic	0.0_460	3.4260	0.0446
o Brombenzoic	0.0_2145	1.8564	0.3254
m "	0.0_3137	0.4023	0.2297
p "	0.0_4835	0.0564	0.4168
α Bromcinnamic . . .	0.0144	3.9325	0.5864
β "	0.0_393	0.5255	0.4640
Cuminic	0.0_450	0.1519	0.2060
o Iodbenzoic	0.0_2132	0.9518	0.4392
m "	0.0_3163	0.1163	0.4408
o Nitrobenzoic	0.0_2616	7.3795	0.3101
m "	0.0_3345	3.4140	0.1217
p "	0.0_3396	0.2771	0.3836
Salicylic	0.0_2102	2.2614	0.2203
o Toluic	0.0_3120	1.1816	0.1108
m "	0.0_4514	0.9801	0.0809
p "	0.0_4515	0.3454	0.1326
o Chlorbenzoic	0.0_2132	2.0868	0.2690
β Naphthoic	0.0_4678	0.0580	0.3590
Cinnamic	0.0_4355	0.4911	0.0982

TABLE XII.

Electromotive force in volts of cells of the type C | A sol. | B sol. C where C, C are inert electrodes and A and B bodies which by their reaction change the electric charges on the ions. In general, solutions contain $\frac{1}{3}$ grammolecule in 1 liter, and are acid, neutral, or alkalin, aqueous solutions.

	$KMnO_4+H_2SO_4$	Cl_2. KCl	MnO_2. HCl	$KIO_3+H_2SO_4$	Br_2. KBr	$KClO_3+H_2SO_4$	$H_2Cr_2O_7$	Br_2. KOH	$KClO_4+H_2SO_4$	HNO_3	Fe_2Cl_6	Cl_2. KOH	$KNO_2+H_2SO_4$	$K_2Cr_2O_7$	$K_3Fe(CN)_6$	I_2. KI	$K_2Fe(C_2O_4)_2$
$SnCl_2KOH$	2.061	1.969	1.931	..	1.723	..	1.697	1.618	..	..	..	1.486	..	1.366	1.285	1.190	..
Na_2S	1.855	1.758	1.721	1.578	1.519	1.506	1.486	1.405	..	1.349	..	1.278	1.226	1.154	1.071	0.981	0.988
NH_2OHKOH	..	1.725	..	..	1.480	..	..	..	..	..	..	..	..	1.120	1.039	..	..
$Cr(C_2H_3O_2)_3KOH$	..	1.696	..	..	1.454	..	..	..	..	..	..	..	..	1.094	..	..	..
$C_6H_3(OH)_3KOH$	1.680	1.590	1.546	..	1.348	..	1.316	1.233	..	..	..	..	..	0.984	0.901	0.808	..
$p\text{-}C_6H_4(OH)_2KOH$	1.531	..	..	..	..	..	1.165	..	..	..	..	..	..	0.828	0.745	..	..
$K_2Fe(C_2O_4)_2$	..	1.379	..	..	..	..	..	..	..	..	..	..	..	0.775	0.692	..	..
$Cr(C_2H_3O_2)_3+KOH$	..	1.301	..	..	1.058	..	1.028	..	..	..	..	..	..	0.696	..	..	..
$K_3Fe(CN)_6$	..	1.190	..	..	0.948	..	0.925	..	..	..	..	..	..	0.589	..	..	..
$I+KOH$	..	1.178	..	..	0.934	..	0.905	..	..	..	..	..	..	0.572	0.494	..	..
$SnCl_2$. HCl	1.265	1.171	1.129	..	0.928	0.920	0.900	0.819	..	..	..	0.688	..	0.566	0.486	0.392	..
K_3HAsO_3	1.256	1.160	1.122	..	0.918	..	0.889	0.809	..	..	..	0.679	..	0.556	0.478	0.383	0.343
NaH_2PO_2	..	1.152	..	..	..	..	0.879	..	..	..	..	..	..	0.545	..	..	..
Cu_2Cl_2	1.203	1.104	..	..	0.865	..	0.836	..	..	..	..	..	..	0.503	..	..	..
$Na_2S_2O_3$	1.189	1.088	..	..	0.846	..	0.820	0.736	..	..	..	0.607	..	0.487	0.407	0.311	..
Na_2SO_3	1.181	1.082	1.043	0.905	0.839	0.830	0.812	0.729	0.682	0.672	0.654	0.601	0.556	0.478	0.399	0.304	0.263
Na_2HPO_3	..	1.071	..	..	..	..	0.802	..	..	..	..	..	..	0.469	0.390	..	..
NH_2OHHCl	..	1.028	..	..	0.786	..	..	..	..	..	..	..	..	0.425	0.345	..	..
$NaHSO_3$	1.100	1.001	0.962	0.826	0.758	0.752	0.733	0.651	0.603	0.594	0.575	0.524	0.474	0.400	0.318	0.225	0.182
H_2SO_3	1.044	0.946	..	..	0.705	..	0.679	0.596	..	..	..	0.469	..	0.345	0.263	0.171	..
$FeSO_4H_2SO_4$	0.968	0.875	..	..	0.628	..	0.602	..	..	..	..	..	..	0.268	0.191	0.092	..
$K_4Fe(CN)_6$	1.168	1.070	1.033	0.894	0.828	..	0.801	0.719	0.671	0.661	0.642	0.589	0.544	0.467	0.387	0.294	0.252

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